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## An experimental study of crystallization in opal glass

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AN EXPERIMENTAL STUDY OF CRYSTALLIZATION

IN OPAL GLASS

BY

WILLIAM C. ROUS, JR.

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A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

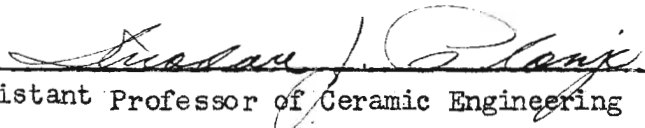
MASTER OF SCIENCE, CERAMIC ENGINEERING

Rolla, Missouri

1950

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Approved by   
Assistant Professor of Ceramic Engineering

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To Dr. Wm. J. Knapp who suggested the use of quenches and the x-ray spectrometer in a study of crystallization in opal glass, to Professor T. J. Planje who suggested the measurement of electrical conduction of the glass at various temperatures, and to Dr. P. G. Herold for his constructive criticism the author expresses his appreciation and gives due credit.

For her help and encouragement, the author wishes to express his appreciation to his wife, Jane Rous.

W.C.R.

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## INTRODUCTION

Opal glasses are well known from use in such forms as ointment jars, lighting globes, wall panelling, and decorative effects in glass vases. Cryolite, fluorspar, and sodium fluosilicate are used in varying proportions in most glasses of this type. Since little is known of the mechanism of crystallization in opal glass, there is a definite need of gathering further information on this subject. This information is of particular interest to the manufacturers whose products consist of this type of glass. Further information would aid in control of the characteristics desired and perhaps would allow a more economical control.

In true Opal glasses the particles which scatter light are of diameters ranging from 0.4 to 1.3 microns and number from <sup>10</sup>10 to <sup>14</sup>10<sup>14</sup> per cubic centimeter (p. 224 of Scholes "Modern Glass Practice"). Since opacity is due to the large surface area of the inclusions within the glass, Opal glasses can be considered a solid sol in the upper colloidal size range.

Probably the best single general reference on Opal glass is "The Past and Present Practice and Theory of Opaque Glass" by C. H. Commons, Jr. published in the Bulletin of the American Ceramic Society, September 15, 1948.

A statement of an ideal outline of action would be:

1. Take a glass with as few variables present as feasible, and determine at what temperature the crystals begin to form, when growth stops, and rate and size of formation of crystals in Opal glass.

2. Determine effect of variation in cooling rate on crystal properties mentioned above.

3. Compare with two commercial glasses and obtain chemical analysis of the three glasses.

4. Obtain the above information melting glass in a standard geophysical crystallizing furnace (as described in Jour. Amer. Cer. Soc., p. 320, 1938), then with set known cooling schedules quench the batch at various temperatures.

5. Run x-ray diffraction patterns on quenched batches and analyze the results.



## REVIEW OF LITERATURE

(1)

Opal glass is a term which often includes Opalescent and Alabaster glasses as well as the true opal glasses. This broader meaning is usually understood because all of these glasses have internal structures which cause light falling on them to be scattered. As a result, they appear white to the eye and are characterized by translucency without transparency. They are well known from their use in such forms as ointment jars, lighting globes, table tops, wall panelling, etc. The name Opal glass, however, in its exact and exclusive meaning is applied to glasses of the light diffusing type which do not directly transmit light. On looking at a lighted lamp filament through such a glass, the outline cannot be detected; but if the thickness of the glass is sufficiently reduced, the outline of the filament is seen to be sharply delineated, as an image of reddish color. A glass which shows this reddish outline of the filament when viewed through its normal thickness, and which also appears to be white by reflected light may be more properly called opalescent glass. In contrast, Alabaster glasses show the outline of a filament without markedly modifying its color when it is viewed through them (or through sections of reduced thickness).

All of these types of glasses have their characteristic light-

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(1) Scholes, S. R. Modern Glass Practice, Industrial Publ. Inc., Chicago, 1935, BLAU, p. 224, 139 and 271.

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scattering properties because they contain, embedded within the glass, many tiny inclusions which have different indices of refraction from that of the glass itself. Light, on passing through such a glass is scattered by encountering these inclusions with resulting reflection, refraction, or diffraction. Blau (in the book "Modern Glass Practice" by Scholes, p. 224) states that in true Opal glasses these particles are of diameters ranging from 0.4 to 1.3 microns and number from  $10^{10}$  to  $10^{14}$  per cubic centimeter. Since a true colloidal dispersion has particles within the arbitrary range of 0.5 micron to 1.0 millimicron, opal glasses would be considered a solid sol from within the upper range to a particle size slightly larger than the range of the colloidal classification. Opal glass may be considered a colloidal system because its opacity is due to the large surface area of the inclusion within the glass. Although the particles constitute less than 4% of the mass of the glass itself, these inclusions cause light passing through the glass to traverse a distance of from 4 to 8 times the thickness of the pieces. In general, the Alabaster glasses contain inclusions of larger dimensions and of lower numbers per unit of volume. In these various glasses the inclusions vary in character from gases (minute bubbles) to amorphous solids and small crystals.

It is necessary to use special compositions and proper conditions to produce internal glass-structures of the types described. The compositions require quantitative relations of the commoner glass making oxides plus the presence of additional constituents such as: Fluorides, Chlorides, Sulphates, Phosphates, Oxides of Tin,

Zirconium, Titanium Antimony, etc. Of these listed, the glasses containing the fluorides are of the greatest commercial importance. They usually are produced by introducing fluorspar or cryolite into the glass batch. Typical analyses of such glasses are as follows:

	<u>Common Opal</u>	<u>Opal for Lighting Ware</u>
$\text{SiO}_2$	65.8	64.0
$\text{Al}_2\text{O}_3$	6.6	4.2
$\text{ZnO}$	---	8.5
$\text{CaO}$	10.0	5.6
$\text{K}_2\text{O}$	9.6	1.5
$\text{Na}_2\text{O}$	3.8	12.0
$\text{F}_2$	5.3	7.3

The proper determination and control of the time-temperature relations of melting, working and cooling glasses of this type, are of the greatest importance. This is essential during melting and refining because the fluorides are lost from the melt as the alkaline fluorides, hydrogen fluoride, and silicon tetra-fluoride. When molten, these glasses are transparent, and only during the cooling do the inclusions separate out. X-ray diffraction studies have indicated that these inclusions are crystals of calcium fluoride, sodium fluoride or forms of silica. The rates and temperatures of cooling largely determine the dimensions and character of these tiny crystals, in accordance with the principles of crystalline growth (Tammann Theory), (Ind. Eng. Chem., 1933, p.849).

The normal behavior of a liquid, upon being cooled to its

freezing temperature, is to solidify in regular, geometric solids called crystals. This involves a rearrangement of molecules into a definite pattern. If, at the freezing temperature, the liquid possesses enough internal friction (viscosity) the molecules cannot with facility assume the definite positions required by crystal-structure. It is the viscous liquids, therefore which become glassy solids on cooling; while liquids which are mobile near the freezing point develop crystals. It is of fundamental importance to glass-making that molten silica is a highly viscous liquid, and retains this property, or confers it when it is fused with basic oxides.

Ideas about the state of affairs in liquids are not very definite. In the discussion of water solutions of electrolytes we make certain postulates, as to the presence of ions and of undissociated molecules of solute, which seem justified because the behavior of these dissolved substances is very well explained by this theory of ionic dissociation. When we consider other liquids, for example solutions of non-electrolytes, there is no clear-cut theory of constitution. From the behavior of the solution toward electricity, ordinary commercial glass is found to be ionized quite well. Its conductivity is so badly hampered by high viscosity that at ordinary temperatures it is one of the best of insulators (poorest conductors) but at higher temperatures the sodium ions migrate quite freely. However, all this gives no clue to the character of the undissociated compounds which may also be present.

A number of complex silicates can be made to crystallize from soda-lime glasses of definite compositions. Some of these compounds

melt incongruently; that is, they decompose into simple silicates which melt separately. The formation of definite crystalline compound as a devitrification product is no evidence of its existence in the glass. Workers in the field seem to believe that the structure or "lattice" of glass consists of open chains of silicon atoms, widely spaced, and linked together by the oxygen atoms, four of which are considered as surrounding each silicon atom. The atoms or ions of other oxides are considered as occupying the spaces in the loose rambling silica structure.

It should be pointed out, however, that we cannot go too far in assuming that oxides like soda and lime are merely packed in the open spaces of the silica lattice without making assumptions at variance with the physical facts. If soda and lime could be merely packed into the free space in the silica lattice, it is clear that the density of the commercial glasses would be much higher than the observed values. The density of these glasses is more nearly an additive property than is any other physical characteristic. Therefore the silica lattice must, at least, open out and expand as other oxides are added, even if a postulation is not made stating that any actual chemical combination takes place.

(2)  
Peters and Cragoe, and other workers, have found a peculiar break in the curve produced by plotting the expansion of a glass against temperature. This curve shows a sharp upward bend just below

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(2) Ibid.

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the softening temperature. For a time this was thought to represent a critical temperature, constant for a given composition, which represented some definite internal rearrangement of the structure of the glass. Littleton has shown that this is not a definite temperature, but that it depends upon the previous heat treatment of the particular glass. It depends upon what internal structure has been "frozen" during the annealing of the glass.

(3)  
L. M. Angus-Butterworth ("The Manufacture of Glass", 1948) divides opal glasses into two main classes. First, that in which the opacifying agent dissolves, leaving the glass transparent while molten, but causing it to become opaque on cooling. Second, that in which the opacifier never wholly dissolves, but remains very evenly and finely distributed throughout the molten metal. In one type the glass is quite transparent when gathered from the crucible, and gradually becomes opal as it cools. In the other the metal is already opal upon gathering, but becomes more so as the temperature falls.

In most opal glasses the opacity is dependent upon the separation of either finely divided silica or some metallic oxide or both from the mass of glass. The separation is assisted by the presence of fluorides and phosphates. A certain degree of opalescence may result from the separating out of the fluoride (say as aluminum fluoride) or the phosphate themselves from the glass, but as a rule

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(3) C. R. Angus-Butterworth, Pitman Publ. Co., 1948, p. 56.

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the batch is such that they remain combined as fluosilicates and phosphosilicates, throwing out of solution the silica. The source of opal color in glass may be either excess of silica; excess of some metallic oxide such as alumina, tin or antimony, or the presence of fluorides or phosphates.

The most commonly used materials for producing opalescence are feldspar and fluorspar. The batch composition varies greatly, partly in accordance with the degree of opacity required, but the following may be given as examples of typical melts:

Milk-white glass — sand 100 parts, soda ash 15, felspar 13, fluorspar 9, cryolite 8, tin oxide 4.

Alternative milk-colored glass — sand 100, soda ash 12, potash 5, feldspar 15, fluorspar 10, saltpeter 2, cryolite 10, nickel oxide 4.

Enamel-white glass — sand 100, potash 20, saltpeter 5, tin oxide 12, red lead 80, borax 4, bone ash 12.

Opalescent glass — sand 100, soda ash 30, feldspar 34, fluorspar 18, red lead 6, nitre 4, borax 0.5.

Imitation mother-of-pear — sand 100, soda ash 25, red lead 15, salt peter 25, cryolite 1.5, bone ash 5, borax 25, nitrate of bismuth 3, nitrate of copper 0.25, fluorspar 1.5.

Opal glass for illuminating ware — sand 100, soda ash 30, fluorspar 20, felsapr 35, cryolite 8, manganese 0.25.

(4)  
Duval d'Adrian of Washington, Pennsylvania, has recently

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(4) Ibid, p. 57.

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sought to show that, by using complex fluorides of silicon, boron, tin, zirconium, and titanium with the fluorides of the alkaline earths and heavy metals, and adding various mixtures of these to an ordinary glass batch, more satisfactory results are obtained than with simple fluorides. An example of a batch used by him for this purpose is: sand 100, soda ash 35, felspar 20 to 30, magnesium silicofluoride 0.5 to 5, barium stannofluoride 0.5 to 5.

(5)  
Weyl suggests that the technical applicability of tungsten and molybdenum compounds in glasses, apart from serving as constituents of special glasses with high refractive indices, seems to be limited to their use as opacifiers.

Although practically nothing is known of the ultimate nature and constitution of glasses, many useful conceptions result from a consideration of the binary and ternary equilibrium diagrams of the principal glass-forming oxides. G. W. Morey and N. L. Bowen, for example, in their study of the system sodium metasilicate-calcium metasilicate-silica, have shown that commercial glass composition containing  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and  $\text{CaO}$  lie within a triangle formed by the three phases —  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  —  $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 3\text{SiO}_2$  —  $\text{SiO}_2$ . Compositions within this area solidify at the ternary eutectic ( $\text{CaO}$  5.2%,  $\text{SiO}_2$  73.5%, Temp.  $725^\circ$ ).

The glass compositions showing the least tendency towards devitrification are near this ternary eutectic, and the low temperature

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(5) Ibid.

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of this eutectic means that glasses can be held and worked at temperatures where the viscosity is high without devitrification resulting. In commercial glasses, the system is much more complex, but the conception is one of fundamental importance. In practice, it means that the composition of a glass is so adjusted that it can be maintained in a temperature region in which the viscosity is suitable for working and in which there is no tendency to precipitate crystals. In opal glasses, however, additions such as fluoride, intentionally made so the glasses do precipitate crystals at or near the working temperature.

The identification of the particles which cause the diffusion and scattering of incident light has evoked much controversy. J. W. Ryde and D. E. Yates <sup>(6)</sup> have shown, however, that these particles, in fluoride opals, are calcium or sodium fluoride. But apart from the constitutional aspect of opal glasses there is the important practical factor — the occurrence of brittleness — which worries the glass manufacturer.

Recently (that is about 1927) G. Gehlhoff and M. Thomas <sup>(7)</sup> published interesting data showing that, for the particular glass they worked, the production of brittleness was connected with the thermal change point associated with the precipitation of the fluoride. The conclusion drawn was that fluoride opal glasses must necessarily be

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(6) J.W. Ryde and D.E. Yates, Opal Glass, Crystal Growth and Impact Brittleness, Jour. Soc. Glass Tech., Vol. 10, 1927, p. 363.

(7) G. Gehlhoff and M. Thomas, Brittleness of Opal Glass, Trans., Jour. Soc. Glass Tech., Vol. 11, 1927, p. 347.

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worked at a temperature above which the fluoride precipitation occurs if brittle glass was to be avoided.

The experimental data here given resulted from an attempt to correlate the contradictory results which were obtained in the manufacture of various opals, some of which results did not coincide with the generalization of Gehlhoff and Thomas. To illustrate the general conclusions arrived at, it is only necessary to discuss three particular opals. The three glass chosen for illustration are A, B, and C, and the chief characteristics are tabulated.

Table I.

Opal	Temp. at which viscosity equals $10^{10}$ poises	Normal Crystall- ine phase (X-ray Exam.)	Remarks
A	619°	$\text{CaF}_2$	Brittle when gathered under 1050°
B	585°	$\text{CaF}_2$	Brittle at low and high gathering temperature
C	625°	$\text{CaF}_2$	Occasionally brittle at low temperatures.

(8)

In an article by J. F. Hyslop, it was pointed out that brittleness is intimately associated with the tendency of the opal to produce angular crystals. These may be produced:

(a) by working the glass in the devitrification range of the matrix glass, or

(b) by using a glass of too high fluidity which permits the growth of angular fluoride crystals.

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J.F. Hyslop, Opal Glass in Crystal Growth, Jour. Soc. Glass Tech., Vol. 11, 1927, p. 362.

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The main facts brought forward by Hyslop:

1. It was shown that the fluoride particles in an opal glass are globular if the viscosity of the glass is high. With low viscosity the particles assume characteristic crystalline form.

2. It was also shown that, in an opal heated under the critical point found by Gehlhoff and Thomas, the logarithm of the particle size is directly proportional to the reciprocal of the absolute temperature. That is, the particle size, for equal times of heating under the critical point, is inversely proportional to the viscosity of the glass.

3. Impact brittleness in opal glass is associated with several factors. The chief cause of brittleness is the tendency of the glass to produce sharp angular crystals and these may be formed by:

(a) the tendency of the matrix to precipitate silica. If the opal is susceptible to this secondary devitrification, a careful choice of working temperature is necessary if the absence of brittleness is desired.

(b) the tendency of the glass to grow angular instead of globular fluoride particles. This happens in a glass of low viscosity and such a glass is brittle at low and high working temperatures.

Impact brittleness has in one instance been associated with heterogeneous glass and in this connection it is shown that the size of cullet is an important factor in the production of a homogeneous glass.

(9)

W. E. S. Turner states the condition for the formation of the vitreous state is a fixed minimum velocity of cooling. In order to obtain as a final product a structure which contains so few molecules in the crystalline state that it still may be spoken of as glass (amorphous), it is necessary to hurry through the dangerous temperature range in the neighborhood of the greatest velocity of crystallization and the maximum formation of spontaneous nuclei, with a minimum velocity of cooling.

When a crystal is heated gradually, it begins to melt at a definite temperature. At this temperature it may remain in equilibrium with its melt for an indefinite period.

As a rule, a crystal, on heating, begins to melt at a definite temperature, independent of the rate heating, and, generally speaking, a crystal cannot be superheated except in the case of certain crystals whose rate of formation is very slow, and these melt consistently. Fused crystals behave quite differently on cooling. If the melt is cooled slightly below the temperature of the melting point, crystallization does not take place, and undercooling occurs. The melt may remain a shorter or a longer time in this undercooled state. If crystallization follows, it begins at individual points in the supercooled liquid. A crystallization center is formed which may grow to a single crystal, or, as very frequently happens, from which fine needle-shaped crystals grow in all directions and form a spherulite

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(9) W.E.S. Turner, Soc. Glass Tech., Dranall Road, Sheffield, 1927, Richard Clay and Sons, Ltd., Bungay, Suffolk.

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The capacity of a liquid for supercooling is determined by two factors:

1. the number of crystallization centres formed in unit volume in unit time, and
2. the linear rate at which the ends of the needle crystals grow into the supercooled liquid.

(10)

Gustav Tammann has probably done more than any contemporary worker on the fundamental theories of crystallization. He points out:

1. A vitreous solid is fundamental, different from a crystalline solid, at least several of the properties are dependent upon direction; in a glass, as in a liquid or a vapor, all of the properties are independent of direction provided that the glass be made free from inner strain by prolonged cooling. The properties dependent upon direction are designated as vector properties, those independent of direction as scalar. Therefore, crystals are differentiated from gases, liquids, and vapors by the fact that at least a portion of their properties are vector whereas the properties of glasses, liquids, and vapors are scalar throughout.

2. The states intertransformable in a continuous way are designated as isotropic, whereas the anisotropic are states continuously transformable neither into each other nor into the isotropic state. (The behavior of any one substance such as water, may be used as a comparison to test the division of the states of aggregation into the

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(10) G. Tammann, States of Aggregation, D. Van Nostrand Co., N.Y., 1925, pp. 1-5, 226, 233, 236, 82, 36, and 125. Trans. by R.F. Mehlk, St. Louis Library.

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gaseous, the liquid, and the solid.)

3. The amount of inner friction (viscosity) is likewise often taken as a basis for the distinction between the term "solid" and the term "liquid".

4. The melting of crystals of different substances produces liquids of different internal friction (viscosity) and the magnitude of the viscosity of the molten product can be of the same order as that of the crystal, as shown by silica and the acid silicates.

5. On the other hand, crystals can be so weak that their surface tension can influence, and even determine, their crystalline form. The kind and the manner of the change from states whether continuous or not is important.

In many undercooled liquids the number of crystallization centers formed in a unit of mass per unit of time is so small that with small linear transformation velocity it is easily possible to count them and to study the influence of different alterations upon them. It has been found that the tendency towards spontaneous crystallization is highly sensitive to slight alterations in the undercooled liquid (such as may be caused by admixture), and that there exists a pronounced temperature maximum.

In order to count the number of crystallization centers the liquid is first warmed in a closed tube to a temperature above the melting point and is then placed for a given time in a bath of known temperature. Crystallization centers are thus formed, which, however, are not visible because of the low crystallization velocity obtained at this temperature. In order to make visible these centers of crys-

tallization it is necessary to develop them which may be done by warming the undercooled liquid to a higher temperature at which the number of centers is disappearingly small but at which the crystallization centers grow to visible structures which may easily be counted.

The ability to undercool persists in the salt of the acid anhydrides, and is the greater, the smaller the amount of the basic oxide combined in the salt. The acid silicates and borates, for example, may be obtained in the glassy state with slow cooling, and the same is true of the salt of metaphosphoric acid. The more basic the silicate or borate, the more rapidly must it be cooled in order to obtain it as a glass.

For the process of forcing of spontaneous crystallization a temperature gradient is produced in a column of the vitreous liquid which is to be investigated, within which lies the temperature of the maximal nuclei number. Under these conditions crystallization becomes noticeable after some time by the appearance of turbidity in the clear mass in the neighborhood of the temperature of the maximal number of crystallization centers. In time this turbidity proceeds towards both ends of the liquid column and crystallites visible to the naked eye sometimes form. If the liquid column is contained in a glass or perhaps silica tube, it is merely necessary to break the tube at the point at which the turbidity exists in order to obtain a few crystallites, and to use these to inoculate the mass in which crystallization is to be forced, at a temperature somewhat higher than that which prevails in the temperature gradient at the place of turbidity. By vig-

orous stirring the whole mass can be brought to crystallization at this temperature. (P. 235 of Tammann's "States of Aggregation", 1926 show curves illustrating this type.)

In as much as the process of spontaneous transitions is an atomic one it will be subject to the laws of probability. Therefore, only the probability of the formation of crystal-centers, the forms of which have different stability, may properly be discussed. Ordinarily, however, grains of the forms with different stability appear simultaneously. The relation between the number of grains is very sensitive to the presence of foreign substances. Often times one recrystallization is sufficient to change this relation considerably, and in some cases the effect is so great that the nuclei of one form are no longer observed. The grains of the more stable as well as the grains of the less stable may disappear in this way.

It has been pointed out that the temperature of the maximal nuclei number does not greatly change in consequence of admixture. It might be expected, therefore, according to the "Law of Stages", that with one and the same substance the temperatures of these maxima would decrease with increasing stability of the forms concerned.

The atomistic conception of the formation of crystallization centers leads to the assumption that the nuclei number increases with increasing undercooling from very small values immediately below the melting point. It has been maintained, however, that the nuclei number is actually zero within a certain temperature interval below the melting point, and that it begins to increase only after the passing of this interval. This temperature interval has been designated



as the sphere of metastability, and in its only contact with the solid phase has been thought sufficient to bring about crystallization. A limited metastability of a few tenths of a degree must exist because of the increase in solubility resulting from decrease in particle-size.

As for the influence upon the number of crystallization centers of the temperature to which the melt is heated before undercooling — if the process of crystallization actually consists of two processes, the first of which is the loss in energy by the molecules in becoming anisotropic, and the second, the arrangement of the molecules upon a lattice, — it is possible that a small number of anisotropic molecules exists in an undercooled melt. If this be the case, the number of crystallization nuclei formed with a given degree of undercooling must be a function of the temperature to which the melt is heated before undercooling, and must decrease with increase in this temperature.

The number of crystallization centers which form with a definite undercooling is usually directly proportional to the time. The probability for the formation of a center of crystallization in an undercooled melt is extremely small in comparison to the number of molecules present (change in viscosity with undercooling). The fact that crystals are polyhedra indicates that the Linear Crystallization Velocity (C.V.) must be dependent upon direction; for if it were independent of direction, crystals would be bounded by spherical surfaces. The direction to which any value of C.V. refers is that defined by a line perpendicular to the series of sur-

faces formed by successive additions of atom-planes to an original crystal-face during the growth of a crystal. The distances of the crystal-faces from the center of crystallization have the same relation to one another as the values of the C. V. of the respective faces. There is another crystallization velocity of the character of a vector, determined by introducing the substance into a dilatometer and reading the change in volume in the unit of time. This "three-dimensional velocity", however, depends upon the number of crystallization centers, upon their positions with respect to each other, and upon conditions for the withdrawal of the heat of crystallization. In consequence of this, the determinations do not give consistent results.

The C. V. for each crystal-face is dependent in a characteristic manner upon the conditions existent during formation.

At the beginning of crystallization during cooling the heat of fusion of the melt is set free, and for a time arrests the fall in temperature.

If the temperature of the point of halt upon heating curve differ from that upon the cooling curve there will be a question as to the actual position of the equilibrium temperature. A great amount of undercooling with little overheating would give an average value too low, and the reverse condition too high.

## LABORATORY PROCEDURE

1. A calcium fluoride type of opal glass was selected for study because it is a more prevalent type in commercial use. The simplest type of glass is desirable in order to eliminate as many variables as possible. Therefore, the glass batch selected consisted essentially of  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and Fluorine, — adding all of the Fluorine as Fluorite, the remaining  $\text{CaO}$  as Whiting, the  $\text{Al}_2\text{O}_3$  as  $\text{Al}(\text{OH})_3$ , and the  $\text{SiO}_2$  as Potter's Flint. Some glass batches were used with all of the  $\text{Al}_2\text{O}_3$  and part of the  $\text{SiO}_2$  added to the batch as Florida Kaolin.

Since a glass having the lowest softening point is the most convenient to work with, a number of compositions were compounded and tried to see which one would be more desirable to use.

(1)  
A triaxial phase diagram of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$  was used to determine some probable compositions, and to this 2 to 10% Fluorine was calculated in.

A list of batches tried are shown in Table II on the next page. The batches which were used were D, 4c, and 4n as designated in Table II.

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(1) Journal American Cer. Soc., Nov. 1, 1947, Part II, Phase Diagrams for Ceramists, by Hall and Insley.

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TABLE II

Opal Glass Batch Compositions Tried for Determination of Batches  
Preferable for Use in Study of Crystallization

<u>% Constituent</u>	<u>Batch Composition</u>	<u>Remarks</u>
#1. 68 SiO <sub>2</sub> 12 Al <sub>2</sub> O <sub>3</sub> 13 CaO 7 F <sub>2</sub>	53.9 Potters Flint 30.4 Fla. Kaolin 5.0 Whiting 14.2 Fluorspar	not molten at 1580° C
A. 62.0 SiO <sub>2</sub> 13.25 Al <sub>2</sub> O <sub>3</sub> 14.75 CaO 10.00 F <sub>2</sub>	46.4 Potters Flint 33.5 Fla. Kaolin 20.5 Fluorspar	soft at 1000° C pourable around 1500° C
B. 68.0 SiO <sub>2</sub> 12.0 Al <sub>2</sub> O <sub>3</sub> 13.0 CaO 7.0 F <sub>2</sub>	53.9 Potters Flint 30.4 Fla. Kaolin 5.0 Whiting 14.2 Fluorspar	At 1200° C soft, will not stick to rod
C. 54.6 SiO <sub>2</sub> 13.6 Al <sub>2</sub> O <sub>3</sub> 22.8 CaO 9.2 F <sub>2</sub>	38.4 Potters Flint 34.4 Fla. Kaolin 16.45 Whiting 18.9 Fluorspar	At 1200° C almost soft enough to pour
D. 60 SiO <sub>2</sub> 15 Al <sub>2</sub> O <sub>3</sub> 25 CaO 10 F <sub>2</sub>	42.35 Potters Flint 38.0 Fla. Kaolin 18.3 Whiting 20.55 Fluorspar	Almost soft enough to pour at 1200°, slightly bet- ter than 'C'. Poured at 1250° C.
J. (random cold cream jar):	at 700 degrees softens and deforms under own weight at 1050-1150 glass is clear, almost pourable.  Was still opaque at 900, though very fluid.  Plate of Libbey-Owens decorative panelling: 750-800° C. melts and flows. At 900-950 opacity is disappearing, 1050-1150 still not fluid.	

Table II (continued)

<u>% Constituent</u>	<u>Batch Composition</u>	<u>Remarks</u>
D <sub>3</sub>	44.9 Potters flint 37.2 Fla. Kaolin 17.55 Whiting 8.0 Fluorspar	Too viscous to pour at 1450°C

The best glass to use is #D above, pourable at 1250°C.

2c	58.0 SiO <sub>2</sub> 13.73 Al <sub>2</sub> O <sub>3</sub> 18.81 CaO 2.0 F <sub>2</sub>	58.0 Potters Flint 21.2 Al(OH) <sub>3</sub> 33.6 Whiting 4.12 Fluorspar	1275°, just beginning to fuse in droplets on surface 1375°, very viscous and difficult to pour.
4c	58.0 SiO <sub>2</sub> 13.73 Al <sub>2</sub> O <sub>3</sub> 15.86 CaO 4.0 F <sub>2</sub>	58.0 Potters Flint 21.2 Al(OH) <sub>3</sub> 28.3 Whiting 8.23 Fluorspar	1275°, partly fused 1375°, portion fritted was half flashed, portion pressed mold made a good opal
6c	58.0 SiO <sub>2</sub> 13.73 Al <sub>2</sub> O <sub>3</sub> 12.12 CaO 6.0 F <sub>2</sub>	58.0 Potters Flint 21.2 Al(OH) <sub>3</sub> 22.3 Whiting 13.45 Fluorspar	1275°, molten 1350° poured, frit and pressed glass both was good opal with traces of clear glass

(The following batches were tried to determine the melting temperature of a similar opal of NaF.

2n	69 SiO <sub>2</sub> 6 Al <sub>2</sub> O <sub>3</sub> 23 Na <sub>2</sub> CO <sub>3</sub> 2 F <sub>2</sub>	69.0 Potters flint 7.81 Al(OH) <sub>3</sub> 36.55 Na <sub>2</sub> CO <sub>3</sub> 3.68 Na <sub>3</sub> AlF <sub>6</sub>	1000° begins to fuse 1050° fused down with small lumps unfused material on top 1100 is glassy
4n	69 SiO <sub>2</sub> 6 Al <sub>2</sub> O <sub>3</sub> 21 Na <sub>2</sub> CO <sub>3</sub> 4 F <sub>2</sub>	69.0 Potters flint 6.43 Al(OH) <sub>3</sub> 33.5 Na <sub>2</sub> CO <sub>3</sub> 7.47 Na <sub>3</sub> AlF <sub>6</sub>	begins to fuse at 975° C; fused fused down begins to be molten at 1005°. 1050 fused down with small lumps unfused material on top. 1100 is glassy. 1250 poured glass gave clear frit with opal streak down center, possibly streak down middle due concentra- tion of F <sub>2</sub>

#4 is the most usable glass pourable at 1275°C.

(In the batch designation, the numeral indicates the % fluorine,  
"c" indicates a CaF<sub>2</sub> opal, "n" indicates a NaF opal glass)

2. Differential thermal data on cooling opal glass from the melt will theoretically show exactly at what temperature nuclei formation or crystal growth will begin on cooling, as well as that temperature at which the glass becomes clear upon melting. This should be more accurate than the x-ray data as the crystal cells would have to be a certain size before influencing x-ray diffraction, while the first formation of nuclei should show a differential thermal gradient.

With this in mind several stands and a base of  $\text{Al}_2\text{O}_3$  were cast and fired, a differential thermocouple of platinum and platinum — (2) 10% rhodium constructed for use in a thermal analysis. Two wells were drilled in the alumina base and in one well minus 200 mesh  $\text{Al}_2\text{O}_3$  was placed as a standard, in the other cavity a sample of opal glass in a platinum sleeve was placed. The sample of glass consisted of a raw batch which had been fired, fritted, and ground past -200 mesh. The sample was added in this form as addition of the raw batch would give too much shrinkage when it formed a glass. The batch used here consisted of 58% Potters Flint, 21.2%  $\text{Al}(\text{OH})_3$ , 22.3% Whiting, and 13.45%  $\text{CaF}_2$ . The first two runs went as far as 1240°C, at which time the glass soaked thru the bottom of the post as evidenced by a drop in the pattern almost straight down to the bottom of the graph. The third run held up and on allowing to cool while keeping the temperature recorder operating, the pattern behaved the same as if the surface of the glass fell below the couple junction. On heating of the glass the graph of potential against temperature consisted

of a characteristic upward slope, which was thought to be due to an increase in a difference of temperature between the standard and the glass which was emphasized by the platinum sleeve around the glass. The platinum sleeve was used so that the glass could easily be changed without destroying the cast  $\text{Al}_2\text{O}_3$  base. Runs were then made, omitting the sleeve around the glass, including standards consisting of clear glasses which included coke bottle glass and pyrex tubing. Approximately 15 runs were made with the differential thermal apparatus.

3. A furnace to make quenches of opal glass was constructed, using the article "Standard Geophysical Crystallizing Furnace", Journal American Ceramics Society, p. 321, 1938, and a bulletin titled "Construction of Electric Furnaces for the Laboratory" published by Norton and Co., Oct. 1942, as a reference.

4. Quenches were made by placing the material in a platinum crucible and placing the crucible in a alundum tube wound with a resistor of iridium free platinum -- 10% rhodium wire 0.8 millimeters in diameter. The crucible is suspended with a platinum wire. Two thermocouples from platinum and platinum alloyed with 10% rhodium were placed in adjacent holes drilled in a cylinder of cast  $\text{Al}_2\text{O}_3$  (3) The  $\text{Al}_2\text{O}_3$  cylinder was then placed as close as possible to the surface of the sample without touching the surface. One thermocouple was hooked up to a Brown recording potentiometer, the other couple

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(3) W. E. Haurth, Jr., Slip Casting of Aluminum Oxide, Jour. Amer. Cer. Soc., Vol. 32, No. 12, Dec. 1, 1949.

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was attached to a Leeds and Northrup manual potentiometer from which a temperature check on the first thermocouple reading was made. After heat treatment the reading of the final temperature was held constant for 15 minutes at which time the crucible was dropped into a gallon crock of water. The water was agitated by blowing air through a tube placed about an inch from the bottom of the crock. The sample was then taken, ground in a mortar and pestle, screened, and an x-ray powder sample run on the North American Phillips X-ray spectrometer. A reference on the Geiger-Muller X-ray spectrometer by F. G. Firth may be found on page 108, Vol. VI of Alexander's "Colloid Chemistry".

In taking the x-ray diffraction pattern a copper target, nickel filter, and a 2 r.p.m. motor to rotate the scanning arm on the goniometer was used. After a pattern was obtained, an average line was drawn through the background, and the intensity of each peak measured from its average background. The Hanawalt procedure<sup>(4)</sup> was then followed for a qualitative determination of the sample using the A.S.T. M. card index of X-ray powder diffraction data of intensities and d values.

5. Photomicrographs were taken of glasses 8, 9, 19, 23, 24, 26, 27, 28, 30, 31, 35, 37, 38, 43, 44, 48, 49, 50, 55, 56, 59, 60, 63, 64, 67, 69, 74, and 75. A 3.2x objective was used with a 5x ocular, the image being projected on 4 x 5 inch kodak super pancho-press type B sheet film. This arrangement gave a magnification of

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(4) Ind. and Eng. Chem., Anal. Ed., Vol. 10, 1938, p. 457.

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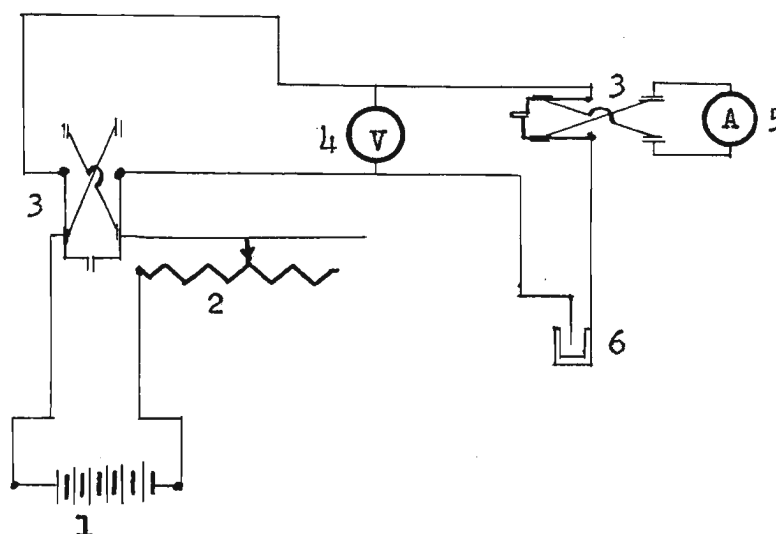


approximately 60x in the negative. After the image was printed on Ansco cykora paper the magnification of the photographed grain was approximately 50x. Two 4-watt white General Electric six-inch fluorescent bulbs on one reflector, and a Mazda 6-volt, 18 amp. GE bulb on another reflector were used for illumination.

6. A sample of opal glass of the composition of 4n was fritted clear and placed in a platinum crucible which had a platinum lead welded to it. An alumina lid was made to fit the top of the crucible and a hole drilled in the center of the lid. A platinum probe was then placed in the center glass approximately one centimeter from the bottom and bent so as to maintain this distance in the center of the crucible. The cylinder of alumina containing the two thermocouples was then placed on top of the lid and the assembly placed in the platinum wound furnace. The platinum leads were hooked to a knife switch and a circuit of a car battery in series with a Welch rheostat (57 amp., 1300 ohm) and a Welch D.C. milliammeter (range 0-150 mils) and in parallel with an RCA Electronic Voltmeter. This arrangement was set up to determine the difference in current flow versus the temperature of the glass. Theoretically the amperage will increase linearly with an increase in temperature until the material which causes the opacity begins to dissociate at which time there will be a sharp jump in amperage compared to the increase in temperature. When the material has completely dissociated the amperage will increase with temperature at approximately the same rate as before the dissociation began. Runs were made with an A. C. circuit as well as with a D. C. circuit.

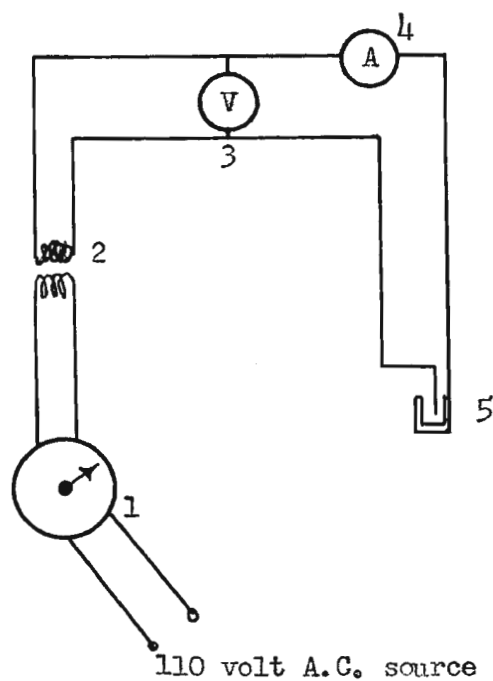
Figure 1

D. C. Circuit Used For Measurement Of Change Of Conduction Of Current Through Opal Glass With Change In Temperature.



1. Automobile storage battery
2. Welch Rheostat (57 amps, 1300 ohms)
3. Double throw, double pole knife switch
4. RCA "VoltOhmyst"-Electronic Voltmeter
5. D.C. milliammeter (range 0-500 mils)
6. Platinum crucible containing opal glass with platinum probe in glass one cm. from base of crucible.

Figure 2



A. C. Circuit Used For Measurement Of Change  
Of Conduction Of Current Through Opal Glass  
With Change In Temperature

1. Variable Voltage Transformer  
(American Instrument Co.)
2. "Wizard" doorbell transformer, 5 watt cap.  
(Jefferson Electric Co.)
3. "VoltOhmyst" Electronic Voltmeter
4. A.C. milliammeter (range 0-500mils)
5. Platinum crucible containing opal glass  
with platinum probe in glass one cm.  
from base of crucible.

DATA FROM MEASUREMENT OF CHANGE OF CONDUCTION OF CURRENT  
THROUGH OPAL GLASS WITH CHANGE IN TEMPERATURE

1. Using direct current circuit as shown in Figure 1, not keeping voltage constant, using glass 4n.

(On raising temperature):

<u>Current</u> <u>(mils)</u>	<u>Voltage</u> <u>(volts)</u>	<u>Temperature</u> <u>(deg. centigrade)</u>
10	4.8	498
16	4.5	542
21	5.25	570
30	3.6	640
38	3.2	670
41	3.0	788
0	5.65	824

2nd run with D.C. circuit (raising temperature)

0	5.8	200
0	5.6	480
0.8	5.5	470
2	5.4	586
4	5.2	600
9	4.9	618
11.5	4.7	620
14	4.55	626
25	3.6	656
28	3.4	
31	3.2	662
40	2.7	666
47	2.3	804
50	2.1	716
53	1.9	866
52	1.75	966
50	1.75	980
54.5	1.8	1000

2nd run with D.C. circuit continued (lowering temperature)

<u>Current</u> <u>(mils)</u>	<u>Voltage</u> <u>(volts)</u>	<u>Temperature</u> <u>(deg. cent.)</u>
52.5	1.8	1000
51	1.9	960
45	2.0	940
43	2.2	920
45	2.25	900
35	2.7	870
36	2.75	860
35	2.7	840
34.5	2.75	820
35	2.70	800
37	2.6	780
38	2.5	760
40.5	2.6	730
40.5	2.6	720
41	2.55	700
44.5	2.3	680
36.5	2.8	660
35	2.9	640
32.5	3.0	620
30	3.2	600
21.5	3.7	580
10	4.2	560
6	4.6	540
3.5	4.8	520
2.0	4.9	500
0.9	5.0	480
0.3	5.1	470
0.0	5.1	460

2. Using alternating current circuit as shown in Figure 2, the voltage was maintained constant at 5 volts with a variac. The same glass used with the D.C. runs was used here.

(On raising temperature)

<u>Current</u> <u>(mils)</u>	<u>Temperature</u> <u>(deg. cent.)</u>
50	520
60	560
65	580
75	600
105	620
135	640
170	660
220	680
280	700
420	720
480	740
520	760
480	780
410	800
310	820
300	840
295	860
295	880
275	900
270	920
265	940
275	960
210	980
210	1000
210	1020
210	1040
210	1060

2nd run with A.C. circuit, voltage maintained constant.

(Raising Temperature)		(Lowering Temperature)	
<u>Current</u> <u>(mils)</u>	<u>Temperature</u> <u>(deg. cent.)</u>	<u>Current</u> <u>(mils)</u>	<u>Temperature</u> <u>(deg. cent.)</u>
5	660	480	1100
50	680	420-450	1080
60	700	460	1060
120	720	440	1040
130	740	470	1020
170	760	460	1000
195	780	450	980
220	800	440	960
250	820	420	940
270	840	400	920
280	860	385	900
290	880	370	880
330	900	350	860
370	920	330	840
420	940	315	820
440	960	300	800
470	980	285	780
480	1000	270	760
480	1020	240	740
480	1040	220	720
480	1060	205	700
400-450	1080	200	680
480	1100	175	660
		145	640
		130	620
		110	600
		90	580
		65	560
		50	540
		25-10	520
		0	500

3rd run with A.C. circuit, voltage maintained at 5 volts.

(on Raising Temperature)

<u>Current</u> <u>(mils)</u>	<u>Temperature</u> <u>(deg. cent.)</u>
5	580
10	600
15	620
20	640
70	680
90	720
120	740
160	760
200	780
220	800
250	820
270	840
300	860
320	880
350	900
375	920
400	940
420	960
430	980
430	1000
430	1020

(on Lowering Temperature)

<u>Current</u> <u>(mils)</u>	<u>Temperature</u> <u>(deg. cent.)</u>
430	1020
430	1000
390	980
360	960
340	940
320	920
310	900
290	880
270	860
260	840
250	820
250	800
240	780
220	760
200	740
180	720
170	700
150	680
130	660
110	640
90	620
70	600
50	580
30	560
0	540



PHILIPS GEIGER-COUNTER X-RAY SPECTROMETER DATA  
ON POWDERED SAMPLES OF OPAL GLASS

All samples were run with:

Beam Aperature -- medium; Wedge @ 6

Counter Aperature -- medium: Wedge @ 6

Amplitude 9; Damping 10

Copper radiation, Nickel filter.

In this table the first column contains the 'd' values of the pattern peaks, and the second column contains the intensity of the peak, I, of a sample of glass. The values given for I divided by six equals the height of the diffraction peak in inches. Subsequent columns contain the Hanawalt values, or the A.S.T.M. values, of the substance which match the values of the glass.

The first time a known substance is used the 'd' value is given. When the substance follows in subsequent samples, the 'd' value will be represented by a dash.

\*  
1. Quenched at 900° C.

Ni. Filter		Quartz		CaO, SiO <sub>2</sub> **	
d.	I.	d.	I./I <sub>0</sub>	d.	I./I <sub>0</sub>
7.00					
5.3					
4.24	5.0	4.25	0.25		
3.33	35.5	3.35	1.00		
3.2	1.4			3.22	1.0
3.02	1.0				
2.83	1.6			2.81	0.8
2.45	2.5	2.45	0.15		
2.275	2.5	2.29	0.10		
2.2	1.0	2.23	0.06		
2.12	2.0	2.12	0.09		
—	—				
—	—			1.97	0.8
1.82	5.0	1.82	0.25		
1.662	1.5	1.66	0.08		
1.53	2.5	1.54	0.20		
1.45	1.0				
1.375	5.0	1.375	0.375		
1.255	1.3	1.256	0.03		
1.23	—	1.229	0.04		
1.19	1.4	1.200	0.06		
1.18	1.0	1.180	0.08		
1.15	1.0	1.155	0.01		

\* No. 1 through No. 23 are quenches of glass  
Do

\*\* CaO, SiO<sub>2</sub> - A.S.T.M. Ref. II - 1713

## 2. Quenched at 1000° C.

d.	I	Quartz d.	CaO, SiO <sub>2</sub> d.
7.2	1.4		
6.3	1.0		
5.8	1.5		
5.2	1.2		
5.0	1.0		
4.25	3.0	—	
4.15	4.0		
4.0	1.0		
3.7	1.0		
3.31	22.2	—	
3.18	1.2		—
2.85	1.7		—
2.45	1.3	—	
2.27	2.0	—	
2.12	1.0	—	
1.97	1.2		—
1.82	3.6	—	
1.67	1.0	—	
1.54	6.0	—	
1.375	4.5	—	
1.3	0.5		
1.27	1.2		
1.25	1.1		
1.23	1.0		
1.9	1.0		
1.18	1.7	—	

## 3. Quenched at 1100° C.

		Quartz	CaO, SiO <sub>2</sub>
d.	I.	d.	d.
4.2	10.0	---	
3.32	18.5	---	
3.2	1.0		---
2.85	1.0		---
2.54	1.1		
2.42	2.0	---	
2.27	2.1	---	
2.12	2.6	---	
1.8	2.0		---
1.82	4.0	---	
1.68	1.0	---	
1.55	4.1	---	
1.38	4.4	---	
1.28	1.2		
1.26	1.1	---	
1.2	1.3		
1.18	1.6	---	
1.16	0.6		

## 4. Quenched at 1200° C.

d.	I.	Quartz	CaO, SiO <sub>2</sub>
4.2	4.0	—	
3.78	1.1		
3.33	23.1	—	
3.2	4.0		—
			—
2.45	2.1	—	
2.28	3.0	—	
2.23	1.7		
2.20	1.3	—	
2.12	2.6	—	
1.97	1.4	—	—
1.82	5.0	—	
1.77	0.8		
1.75	0.8		
1.67	1.0	—	
1.65	1.0		
1.54	2.0	—	
1.37	3.6	—	
1.2	1.0		
1.18	1.3	—	

## 5. Quenched at 1225° C.

d.	I.	Quartz	Cristobalite
6.2	1.5		
5.5	1.0		
4.7	4.0		
3.9	3.1		4.04 (1.0)
3.25	22.0	—	
3.12	4.5		3.13
2.72	0.6		2.85
2.45	1.6		
2.27	1.3		
2.12	1.0		
1.97	0.6	—	
1.81	0.3	—	
1.66	0.5	—	
1.58	2.3	—	
1.375	2.1	—	
1.2	0.8	—	
1.10	1.0		

## 6.

5.5	1.0		
4.2	3.6	—	
4.05	3.6		—
3.3	10.6	—	
3.2	1.6		—
2.45	1.0	—	—
2.27	1.1	—	
2.12	1.2	—	
1.98	0.6	—	
1.81	1.5	—	
1.66	1.0	—	
1.58	1.5	—	
1.375	1.5	—	

7.

d.	I.	Quartz	Cristobalite
---	0.6		
5.2	0.5		
4.1	0.6		---
4.0	0.8		---
3.3	3.3	---	
3.1	0.5		---
1.81	2.0	---	
1.58	0.6	---	

8.

		CaF <sub>2</sub>
7.5	1.0	
6.5	1.2	
3.18	1.5	3.15 (0.7)
1.93	1.0	1.93 (1.0)
1.66	0.5	1.65 (0.5)

9. Quenched at 1330° C.

6.7	1.0	
3.15	1.6	---
1.925	1.8	---
1.65	1.0	---

10. Quenched at 1160° C.

6.5	1.0	
5.5	1.0	
4.25	1.0	
3.15	2.0	---
1.925	1.5	---
1.64	0.6	---

11. Heated 1375° C.  
Cooled to 1230° C. and Quenched

d.	I.	Quartz	CaF <sub>2</sub>
10.3	—		
4.25	0.7	—	
3.3	0.5	—	
3.15	2.4		—
1.93	2.4		—

12. From 200 - 1418 - 1282° C.

7.5	0.6	
3.16	2.6	—
1.98	2.5	—
1.66	0.5	—
1.4	0.3	—

13. Raw Batch to 1230°C.

				Cristobalite
4.2	1.1	—		
4.05	1.6			—
3.33	3.5	—		
3.15	2.6			—
2.85	0.3			—
2.46	0.5	—	—	—
2.28	0.4	—		
2.12	0.6	—		
1.94	3.0	—	—	
1.66	0.6	—	—	
1.38	0.4	—	—	



## 14. Quenched at 1230° C.

d	I.	Quartz	CaF <sub>2</sub>	Cristobalite
6.5	0.6			
4.25	0.3	---		
4.05	0.7			---
3.35	1.1	---		
3.1	2.4		---	---
1.95	1.6		---	
1.66	0.3	---	---	

## 15. Quenched at 1260° C.

5.2	0.5			
3.3	1.1	---		
3.2	1.2		---	
1.95	1.2		---	

## 16. Raw batch heated to 1160°C. and quenched

6.5	1.0			
4.25	3.2	---		
4.05	0.6			---
3.75	0.5			
3.35	29.6	---		
3.2	3.0		---	
3.0	1.0			---
2.84	0.9			---
2.47	1.4	---		---
2.28	1.6	---		
2.13	1.2	---		
1.82	2.6	---		
1.66	0.5	---	---	
1.54	1.7	---		
1.37	4.0	---	---	
1.18	1.3	---		

17. Quenched at 1100°C.

d.	I.	Quartz	Cristobalite
7.0	1.0		
4.4	4.0	---	
4.15	0.5		---
3.9	0.4		---
3.4	23.2	---	
3.26	1.5		
3.05	---		
2.9	1.5		---
2.78	---		
2.5	2.5		---
2.30	1.4		
2.25	0.5	---	
2.15	1.1	---	
2.0	1.0		---
1.83	2.3	---	
1.77	---		
1.66	---	---	
1.56	2.0	---	
1.38	2.6	---	
1.228	---	---	
1.26	---		
1.2	0.4		

18. Quenched at 1200° C.

d.	I.	Cristobalite
16.0	0.5	
7.5	0.6	
6.3	2.6	
5.8	1.2	
4.35	19.7	
4.05	4.0	---
3.58	0.5	
2.8	1.6	---
2.55	1.2	---
2.48	0.4	---
2.34	1.0	
2.13	0.5	
1.92	1.2	
1.74	0.5	
1.58	1.1	
1.38	1.4	
1.26	---	
1.18	---	

## 19. Quenched at 1230°C

d.	I.	CaSiF <sub>6</sub>	CaO. Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>
8.2	0.5		
5.2	1.5		5.4
4.9	1.0		5.1
3.88	18.1	3.83	
3.7	4.0		3.7
3.3	0.5		3.4
2.85	1.1		2.84
2.72	1.1		
2.5	0.6		2.41
2.33	1.0	2.30	
2.15	0.4		
1.94	1.7	1.91	1.92
1.77	0.5		1.75
1.61	1.9		1.375
1.55	---		
1.4	1.4		
1.22	---		
1.18	---		

## #20. Quenched at 1280° C.

d.	I.	Quartz	Cristobalite
11.0	1.0		
4.3	0.9	---	
4.1	0.7		---
3.38	10.3	---	
3.2	2.0		---
2.55	---		---
2.47	1.0	---	---
2.32	---		
2.28	0.8	---	
2.25	---	---	
2.15	0.6	---	
2.0	---		---
1.83	1.0	---	
1.675	0.5	---	
1.55	0.5	---	
1.38	1.0	---	
1.26	---	---	

## 21. Quenched at 1300°C.

8.0	0.8	
4.35	0.9	
4.25	---	---
3.38	12.5	---
3.2	2.0	
2.93	---	
2.51	0.7	
2.47	---	---
2.28	---	---
2.24	---	---
2.13	---	---
1.99	---	---
1.84	0.9	---
1.54	0.3	---
1.38	0.5	---
1.28	---	---

## 22. Quenched at 1330°C.

d.	I.	Quartz	Cristobalite	CaF <sub>2</sub>
4.3	2.1	---		
4.1	1.0		---	
3.38	13.6	---		
3.2	2.0		---	---
2.74	1.0			
2.52	---		---	
2.46	1.0	---		
2.28	---	---		
2.23	---	---		
2.13	0.7	---		
1.93	---	---		---
1.82	1.9	---		
1.67	---	---	---	---
1.54	0.1	---		---
1.38	1.5	---		---
1.27	---	---		

## 23. Quenched at 1375°C

		*		
4.3	1.5	---		
4.1	1.0		---	
3.37	10.6	---		
3.2	1.5		---	
2.45	0.4	---	---	
2.3	---	---		
2.14	0.5	---	---	
1.825	1.5	---		
1.55	---	---		
1.47	---	---		
1.38	0.7	---		
1.26	---	---		

\* A.S.T.M. Reference II-1007

24. Quenched at 700°C.

d.	I.	Quartz	CaO, SiO <sub>2</sub> *	CaF <sub>2</sub>
4.21	4.8	---		
3.33	51.5	---		
3.12	10.3			---
3.0	17.4		---	
2.48	2.2		---	
2.44	2.3	---	---	
2.27	4.6	---		
2.22	1.9	---		
2.12	1.3	---		
2.08	1.6			
1.97	1.0	---		
1.91	2.3			---
1.86	1.9			
1.82	5.0	---		
1.66	2.0	---		---
1.54	2.6	---		
1.3	2.5			
1.28	---	---		
1.26	---	---		
1.2	0.6			
1.18	1.1	---		
1.16	---	---		

\* A.S.T.M. Reference 2176

Note: Numbers 24 through 43 are quenches  
of glass 4c

25. Quenched at 810° C.

d.	I.	Quartz	CaO, SiO <sub>2</sub>	CaF <sub>2</sub>
5.6	0.8			
4.2	5.0	---		
3.8	0.6			
3.69	0.5			
3.33	37.6	---		
3.12	5.6			---
3.02	12.0		---	
2.47	2.2	---	---	
1.45	2.0		---	
2.275	3.8	---		
2.22	---	---		
2.12	1.6	---		
2.075	2.0		---	
1.97	1.0	---		
1.92	2.8			---
1.9	2.0			
1.86	2.1			
1.81	6.8	---		
1.66	1.2	---		---
1.58	1.0			
1.54	3.5	---		
1.38	3.5			
1.37	3.3	---		
1.25	---			
1.19	---			
1.18	0.6	---		
1.15	---			
1.112	---			



26. Quenched at 900°C.

d.	I.	Quartz	CaO, SiO <sub>2</sub>	CaF <sub>2</sub>	Cristobalite <sup>*</sup>
5.9	0.7				
4.15	5.6				---
3.8	0.6				
33.3	33.4	---			
3.12	3.4			---	
3.0	4.6		---		
2.69	0.7				---
2.43	1.2	---	---		
2.27	1.7	---			
2.225	---	---			
2.11	---	---			
2.08	1.5		---		
1.97	0.7	---			
1.92	1.4			---	
1.9	1.0				
1.87	---				
1.81	8.0	---			
1.66	1.4	---		---	
1.6	---				---
1.54	2.5	---			
1.45	---	---			
1.38	3.8	---			
1.37	---				
1.26	1.0	---			
1.23	---				
1.19	0.6				
1.18	---	---			
1.15	---				
1.112	---				

\* A.S.T.M. Reference 956

27. Quenched at 1000° C.

d.	I.	Quartz	CaO, SiO <sub>2</sub>	CaF <sub>2</sub>
7.5	1.0			
4.2	4.0	---		
3.33	28.0	---		
3.15	1.0			---
3.05	1.2		---	
2.95	---			
2.76	0.5		---	
2.45	1.2	---	---	
2.275	1.6	---		
2.22	---	---		
2.125	1.2	---		
2.0	---		---	
1.97	0.7	---		
1.925	0.6			---
1.802	4.8	---		
1.66	---			---
1.53	1.7	---		
1.375	2.5	---		
1.26	---	---		
1.19	---			
1.18	---	---		
1.16	---	---		

## 28. Quenched at 1100°C.

d.	I.	Quartz	Cristobalite
9.0	0.6		
4.15	1.0	---	
4.0	1.9		---
3.3	8.1	---	
2.275	---	---	
2.21	---	---	
2.11	0.8	---	
2.07	---		---
1.97	0.6	---	
1.82	0.7	---	
1.67	0.5	---	
1.54	0.7	---	
1.375	0.9	---	
1.26	0.6	---	
1.19	---	---	
1.18	---	---	

## 29. Quenched at 1150° C.

		CaSiF <sub>6</sub>	
3.9	3.2	---	---
2.31	---		
2.3	---		
2.16	---		
1.97	---		

30. Quenched at 1300° C.

d.	I.	Quartz	Cristobalite
4.1	0.9		---
3.41	1.2		
3.38	1.2	---	
2.54	---		
1.84	---		
1.74	---		

31. Quenched at 1350° C. — clear glass

7.0	1.0
6.6	1.3
6.0	1.0
4.4	0.8
2.93	---

32. Quenched at 1360°C. (clear) not quenched air cooled.

4.18	0.7
3.81	---
3.51	0.9
3.33	0.7

33. Clear, 1360° - 1300° C. — amorphous pattern, no peaks

34. Quenched at 1210° C.

4.5	0.6
4.2	---
3.85	0.5
3.17	3.0

35. Quenched at 1210° C. (cooled clear)

d.	I.
8.0	---
7.5	1.0
6.75	1.5
3.25	0.9
7.62	0.5

36. 1200° C. cooled without Quenching clear

7.5	1.0
7.0	1.0
4.5	0.6
3.3	---
2.95	---

37. 1310°C, cooled without Quenching clear

7.4	1.0
5.6	0.6
3.6	---

38. 1400 - 1000°, then air cooled.

d.	I.	Quartz	Cristobalite	Tridymite
11.0	0.7			
7.0	---			
6.8	0.6			
6.2	---			
3.35	---			
2.64	0.8			
2.46				
1.77	1.0			
1.66	0.9			

39. 1100° C., cooled in air

20.0	0.6		
6.25	1.0		
4.3	0.8		---
4.2	---		
4.02	1.3	---	---
3.33	---		
2.85	---		
2.47	1.0	---	
1.82	---		
1.57	---		

40. Quenched at 1300° C.

d.	I.
4.5	0.5
3.7	0.6
3.35	0.9
2.81	0.6
1.66	---

41. Quenched at 1340° C.

11.0	0.5
5.5	0.5
2.8	

42. Quenched at 1375° C.

6.0	0.6
4.6	---
4.45	---
4.52	---
1.98	---
1.88	---
1.67	---

43. 1400 - 1000°, then air cooled

8.0	1.0
6.5	1.0
3.58	
3.54	
3.4	0.5
1.83	

44. Raw Batch heated to 600° C.

d.	I.	$\text{Na}_3\text{AlF}_6$	Quartz	$\text{Al}_2\text{O}_3\text{Na}_2\text{O}, 6\text{SiO}_2$ *	NaF
7.0	0.5				
4.2	8.2		---	4.11	
3.7	1.0			3.78	
3.33	56.0		---	3.22	
2.95	2.2				
2.73	0.5	2.75			
2.64	1.4				2.68
2.55	0.8			2.55	
2.45	3.0		---		2.31
2.36	2.5				
2.32	2.7	2.33			
2.27	4.0		---		
2.225	1.5		---		
2.175	1.0				
2.125	2.0		---		
2.025	---				
1.975	2.3				
1.95	0.4	1.94			
1.875	0.8				
1.815	7.0		---		
1.675	2.5		---		
1.63	1.1	1.60			1.632
1.535	6.2		---		
1.45	2.0		---		1.391
1.375	8.0		---		
1.28	0.4				1.335
1.26	0.4		---		
1.19	1.0				
1.18	1.5		---		
1.16	1.0				1.155

\* A.S.T.M. Reference II-709.

Note: Numbers 44 through 75 are quenches of glass 4n



## 45. Quenched at 800° C.

d.	I.	Quartz	NaF
11.0	1.0	---	
7.5	1.0	---	
6.0	1.0	---	
4.7	---		
4.2	6.7	---	
3.33	29.2	---	
2.45	20.0	---	
2.3	5.5		---
2.27	4.0	---	
2.25	1.0	---	
2.125	1.6	---	
2.02	0.5		
1.975	0.8	---	
1.82	8.0		
1.675	1.4	---	
1.63	2.0		---
1.54	3.4	---	
1.44	---	---	
1.375	2.6	---	---
1.285	---	---	
1.26	0.6		
1.23	0.4	---	
1.19	0.7	---	
1.18	0.9	---	
1.15	---		

46. (#45 at 850° C)

d.	I.	Quartz	NaF
7.6	1.0		
6.0	0.1		
4.85	---		
4.2	2.0	---	
4.0	---		
3.33	16.0	---	
3.21	0.7		
2.45	---	---	
2.31	2.7		---
2.225	---	---	
1.97	---	---	
1.81	3.0	---	
1.675	0.6	---	
1.64	0.7		---
1.54	1.5	---	
1.38	2.0		---
1.375	1.9	---	
1.233	---		
1.19	---		
1.18	---	---	

47. 4Ni - Quenched at 900° C.

d.	I.	Quartz	Cristobalite
15.5	---		
9.8	1.5		
8.6	1.4		
5.6	1.3		
4.7	1.5		
4.6	1.4		
3.33	2.7	---	
3.07	---		
1.97	0.6	---	
1.88	---		
1.82	0.9	---	
1.75	---		
1.67	---	---	
1.53	0.5	---	
1.43	0.4	---	
1.37	0.6	---	
1.26	0.5		
1.24	0.4		
1.22	0.4		

48. 960° C., quenched half clear, one-half opal.

7.2	0.6		
4.8			
4.6			
4.3	2.2	---	
4.0			---
3.7			
3.33	1.11	---	
2.85	0.6		---
2.78			
2.25	0.5	---	

49. 1000° C. - Quenched almost clear

14.0	1.4
7.4	0.1
4.7	0.1
3.49	0.9

50.  $4N_2$  Raw Batch  $675^\circ C$ .

d.	I	Quartz	$Na_3AlF_6$	NaF
9.8	0.5			
6.5	1.5			
4.25	9.5	-----		
3.34	37.3	-----		
2.72	1.5		-----	
2.70	1.0			
2.45	5.0	-----		
2.37	4.5		-----	-----
2.27	3.1	-----		
2.22	2.6	-----		
2.12	3.0	-----		
1.975	1.5	-----	1.94	
1.82	5.4	-----		
1.67	3.0	-----		
1.63	2.0		1.60	-----
1.54	7.5	-----	1.57	
1.45	0.7			
1.375	5.8	-----		
1.34	0.3			-----
1.28	0.5	-----		
1.26	1.3			
1.23	0.2			
1.2	2.0			
1.18	1.0	-----		
1.155	0.6	-----		

51.  $4N_2$  Quenched at 700° C.

d.	I.	Quartz	NaF
7.0	0.9		
4.2	5.0	---	
3.33	19.4	---	
3.0	0.5		
2.65	0.4		
2.45	1.9	---	
2.32	4.0		---
2.22	1.3	---	
2.125	1.2	---	
1.97	1.2	---	
1.82	4.0	---	
1.67	1.5	---	
1.63	2.0		---
1.53	3.1	---	
1.37	4.5	---	
1.34	---		---
1.28	---	---	
1.26	0.5		
1.212	0.3		
1.201	0.4		
1.18	0.9	---	

52.  $4N_2$  - Quenched at  $760^\circ \text{C}$ .

d.	I.	Quartz	NaF
4.15	5.5		
3.3	19.2	---	
2.85	---		
2.7	0.5		
2.43	1.3	---	
2.30	3.2		---
2.27	1.6	---	
2.22	1.0	---	
2.12	1.1	---	
1.97	0.9	---	
1.93	0.3		
1.81	2.9	---	
1.67	2.0	---	
1.63	1.5		---
1.54	3.0	---	
1.37	3.5	---	---
1.28	0.5	---	
1.26	1.0		
1.23	0.6		
1.2	1.2		
1.18	0.9	---	

53.  $4N_3$  Ht. Quenched at  $775^\circ$  C.

D.	I.	Quartz	NaF
7.5	1.0		
7.0	1.2		
4.2	4.7	---	
3.33	29.7	---	
2.76	0.5		
2.46	2.0	---	
2.32	4.5		---
2.25	1.5	---	
2.225	1.0	---	
2.12	2.9	---	
1.97	1.4	---	
1.82	5.4	---	
1.67	1.0	---	
1.65	2.0		---
1.54	3.0	---	
1.37	3.0	---	---
1.3	---		
1.26	---		
1.2	1.0		
1.18	2.3	---	

54.  $\text{Ht}_2$   $4\text{N}_3$ , Quenched at  $810^\circ \text{C}$ .

d.	I	Quartz	NaF
9.2	0.5		
8.3	0.6		
4.25	3.3	---	
3.33	21.0	---	
2.98	0.5		
2.45	2.0	---	
2.32	1.2		---
2.22	1.0	---	
2.12	---	---	
2.2	0.4		
1.98	---		
1.97	2.6	---	
1.82	1.0	---	
1.67	---	---	
1.65	1.2		---
1.63	2.0		
1.54	2.5	---	
1.38	---	---	
1.28	---	---	---
1.26	0.1		
1.2	0.8		
1.18		---	



55. Quenched at 860° C.

d.	I.	Quartz	NaF
10.5	1.0		
8.8	0.9		
6.5	0.5		
4.22	3.3	---	
3.34	11.0	---	
2.8	1.0		
2.47	1.1	---	
2.325	1.5		---
2.275	1.4	---	
2.13	1.2	---	
1.98	0.6	---	
1.825	2.0	---	
1.67	0.6	---	
1.63	0.5		---
1.54	2.3	---	
1.46	---		
1.37	1.5	---	---
1.2	---		
1.18	---	---	

56.  $\text{Ht}_4 \text{ 4N}_3$  - Quenched 910° C.

d.	I.	Quartz
13.5	0.6	
10.8	0.5	
7.2	0.6	
4.2	2.1	---
3.33	20.0	---
3.12	---	
2.8	---	
2.45	1.0	---
2.28	0.6	---
2.12	0.6	---
1.98	0.7	---
1.82	3.0	---
1.67	1.0	---
1.54	2.1	---
1.455	---	
1.37	3.0	---
1.28	---	---
1.26	1.0	
1.23	0.5	
1.2	0.6	
1.18	1.0	---

57.  $\text{Ht}_5 \text{ } ^4\text{N}_3$  Quenched at  $960^\circ \text{C}$ .

d.	I.	Quartz
7.5	1.2	
6.3	1.0	
4.35	1.1	
4.27	1.2	---
3.34	6.2	---
2.45	0.5	---
1.85	1.1	---
1.84	1.6	---
1.38	0.5	---
1.26	---	
1.2	---	
1.18	---	---

58.  $\text{Ht}_6 \text{ } ^4\text{N}_3$  - Quenched at  $1020^\circ \text{C}$ .

6.2	0.6	
---	0.5	
3.35	3.0	---
3.12	0.5	
1.82	---	

59.  $\text{Ht}_1 \text{ } ^4\text{N}_4$  - Quenched at  $1060^\circ \text{C}$ .

8.0	1.6	
7.5	1.0	
4.3	1.0	---
3.35	3.4	---
2.45	0.5	---
1.82	0.7	---
1.33	0.5	---
1.18	0.5	---

60.  $\text{Ht}_2 \text{ 4N}_4$  - Quenched at  $1060^\circ \text{ C.}$

d.	I.	Quartz	Cristobalite	NaF
10.5	1.1			
4.25	0.5	---		
4.1	1.1		---	
3.51	1.0			
3.35	1.1	---		
2.34	0.8			
2.31	0.6			---
1.82	---			
1.28	---			

61. Quenched at  $1100^\circ \text{ C.}$

6.7	1.0
6.3	0.7
4.4	1.2
4.03	
3.33	
1.375	

62.  $\text{Ht}_4 \text{4N}_4$  - Quenched at 1120° C.

d.	I.	Quartz	Cristobalite	NaF
6.2	1.1			
5.7	0.9			
	1.0			
	1.0			
4.4	0.6			
	0.6			
3.4	---			

63.  $\text{Ht}_4 \text{4N}_4$  - Quenched at 1120°C

7.7	1.0			
6.8	1.5			
4.45	---			
4.05	4.3		---	
3.33	3.6	---		
2.85	0.6		---	
2.5	1.2	---	---	
2.32	1.0	---		---
1.5	0.6	---		
1.38	0.5	---		
1.28	---			
1.182	---	---		

64.  $\text{Ht}_1 4\text{N}_5$  - Quenched at  $1180^\circ \text{C}$ .

d.	I.	Quartz	Cristobalite
6.2	1.0		
4.1	0.9	---	
3.4	0.6		
3.3	0.6	---	
3.1	0.5		

65.  $\text{Ht}_1 4\text{N}_6$  - Quenched at  $1100^\circ \text{C}$ .

9.0	1.0		
8.8	0.8		
4.151	0.5	---	
4.1	0.6		---
3.35	4.7	---	
---	0.9		
---	0.6		
1.8	---	---	
1.67	0.5		

66.  $\text{Ht}_2 \text{ 4N}_6$  - Quenched at  $1140^\circ \text{ C.}$

d.	I.	Quartz.	Cristo- balite	NaF	$\text{Na}_2\text{O} \cdot \text{SiO}_2$
7.0	0.8				
6.3	1.0				
	1.9				
	0.6				
3.41	2.0				
3.35	1.2	---			
2.52	0.5	---			
1.45	---				
1.425	---				
1.418	---				
1.18	---	---			

67 thru 68.  $\text{Ht}_3 \text{ 4N}_6$  - Quenched at  $1050^\circ \text{ C.}$

6.6	1.0		---		---
4.1	0.8				
3.4	---				
3.0	0.7				---
1.18	---				

69.  $\text{Ht}_1$  - Quenched at  $720^\circ \text{ C.}$  (Clear before heated,  
after  $\text{Ht}$  turned opal)

8.0	1.0				
4.3	1.0	---			
4.1	1.2				
3.33	---	---			
---	1.0				
2.9	1.0				3.04
2.78	0.5				
2.65	0.5				2.40
2.33	2.1			---	
1.65	1.1			---	
1.174	---				

70. Ht<sub>2</sub> of #69 - Quenched at 820°C

d.	I.	Cristobalite	NaF
8.0	1.0		
5.5	1.1		
4.1	2.1	---	
3.4	0.8		
3.25	0.7		
2.85	0.5	---	
2.5	0.6	---	
2.325	1.5		---
1.82			
1.64	0.6		---
1.54	0.6		

71. Ht<sub>3</sub> - Quenched at 920° C. (Approaching clear glass

7.0	1.0	
6.0	1.2	
4.1	1.6	---
3.95	0.5	
3.40	---	
3.33	---	
2.54	0.7	---
1.88	0.5	
1.37	0.8	

72. Ht<sub>4</sub> - Quenched at 1055° C. Clear with seeds

9.4	1.5
7.8	1.1
7.0	1.0
6.75	1.0
---	---
4.7	0.6
3.35	0.7
3.33	---
2.38	---



73. Ht<sub>5</sub> - Quenched at 430° C. - half clear

d.	I.	Quartz	NaF	Na <sub>2</sub> O · SiO <sub>2</sub>
8.3	1.0			
—	0.9			
3.7	0.5d			
3.35	—			
3.33	—			

74. Ht<sub>6</sub> - Quenched at 550° C. - Opal

8.0	0.5			
5.75	0.5			
4.1				
2.48				
2.35	0.6		—	
1.18				

75. Ht<sub>7</sub> - Quenched at 620° C.

5.4	0.6			
3.2	0.6	—		
3.0	0.7			—
2.325	1.6		—	
1.64	0.6		—	
1.27	—			
1.185	—			
1.13	—			

## DISCUSSION

The differential thermal analyses\* run on glass D<sub>0</sub> gave very erratic results. At times the current from the thermocouple caused by a difference in temperature between the standard and the glass D<sub>0</sub>, was out of the range of the recorder. Fifteen runs were made using a program control to give a uniform rise in temperature for each run. Because all 15 of the graphs (temperature differential between the standard and the sample versus the temperature of the furnace) gave erratic patterns, no definite conclusions can be drawn as to what was the cause of the thermal difference. The determination of exactly at what temperature nuclei formation or crystal growth begins could be made if the experimental difficulty were overcome.

To make the differential thermal set up work on crystallization determinations of a glassy substance, the standard used is most important. The type of standard used in this type of work should, apparently, be a glass of a similar composition to the sample glass. The resemblance of the two compositions would be limited by the rearrangement necessary to have a useable standard glass which would not give rise to crystallization within the limits of the heating and cooling schedules used in the formation of crystals in the sample glass. Also of importance, would be a recorder of sufficient sensitivity and of sufficient range.

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\* Step two of laboratory procedure, this text.

When a small amount of glass of the composition of 2c, 4c, or 6c, was heated to 1350-1375 degrees centigrade and then allowed to drop on a piece of pine an unusual effect resulted. The surface of the glass appeared to assume a metallic appearing coating which varied from a shiny leaden or silvery color to a dull silky leaden sheen. This effect was produced on both a smooth and a rough surface of the glass, the smoother surface having the greater luster. This type of phenomena might be adopted to a method of decoration which would be simple to carry out.

The qualitative analysis of the x-ray diffraction data, obtained from the various quenches mentioned in step four of the laboratory, showed quartz as being the crystal giving the largest diffraction peak consistently throughout the runs made with about five exceptions. Approximately seven of the runs gave an amorphous pattern.

The first seven samples of batch D were made by melting the raw batch in a pot furnace at about 1450°C., fritted, ground, and mixed. A small amount of the clear frit was then folded into a platinum foil and heated to various temperatures, held fifteen minutes and quenched. Samples numbers 8, 10, 11, and 12 were made by taking the frit to a temperature of approximately either 1300 or 1400°C., allowing the temperature to decrease in the furnace to the desired value, holding fifteen minutes, and quenching.

In the first group of seven samples, the intensities of the largest quartz peak ( $d = 3.33$ ) were:

TABLE III

<u>Sample No.</u>	<u>I<sub>0</sub> Quartz Peak</u>	<u>Temp. Deg. C.</u>
1	35.5	quenched at 900°
2	22.2	" 1000
3	18.5	" 1100
4	23.1	" 1200
5	22.0	" 1225
6	10.6	" 1320
7	3.3	" 1425

In the second group (numbers 8 - 12) the crystal indicated by the x-ray pattern was  $\text{CaF}_2$ . In number 11 a faint indication of quartz showed with the  $\text{CaF}_2$  lines. The rest of the runs on batch D were made by quenches at various temperatures on heating up of the raw batch. The resulting crystals were quartz, cristobalite, and  $\text{CaF}_2$ . All of the runs made from batch D were partially opal at the minimum. Samples 8, 9, 10, and 11 were the least opaque, being very translucent to transparent. Number 11 was the best opal of the four. The run in which the raw batch was heated to 1400°C cooled to 1230°C in furnace and quenched gave the densest opacity. Numbers 16 through 22 ranged from a partly fused powder to a semi-vitrified undissolved batch, number 22 resembling a partly fused very fine grained sandstone with a few minute specks of unfused material present. The color of number 22 resembled a somewhat dirty white.

Number 24 began the runs made with batches of the composition of 4c. Numbers 24 through 31 were raw batches of 4c heated to the designated temperature and quenched. Number 24 greatly resembled number 22 in appearance despite a difference in the x-ray pattern and the heat treatment. Number 22 quenched at 1330°C had a relative in-

tensity of the quartz peak of 13.6, of the  $\text{CaF}_2$  peak of 2.0. Number 24 (4c) quenched at  $700^\circ\text{C}$  gave a quartz peak intensity of 51.5, of  $\text{CaF}_2$  an intensity of 10.3.

As indicated by the photomicrograph, numbers 26 and 27 were both partially unfused, number 28 was a good opal, number 29 an opal similar to number 28, but slightly more glassy, number 30 was beginning to develop transparent places, and number 31 was a completely clear glass. The intensities of the peaks for these samples ran as follows:

TABLE IV

Comparison of Diffraction Data of Numbers 26 Through 31

<u>Sample No.</u>	<u>Temp. Deg. C.</u>	<u><math>I_0</math> of Quartz Peak (<math>d = 3.33</math>)</u>	<u><math>I_0</math> of <math>\text{CaF}_2</math> Peak (<math>d = 3.12</math>)</u>
26	900	33.4	3.4
27	1000	28.0	1.0
28	1100	8.1	0
29*	1150	0	0
30	1300	1.2	0
31	1350	0	0

\*(number 29 had a cristobalite peak,  $d = 4.0$ , of  $I_0$  equal to 3.2)

Numbers 32 through 43 were samples of a clear glass of batch 4c which were given various treatments in an effort to produce a good opal from the clear frit. Numbers 32 through 37 were all clear glasses. Number 38, as shown in the photomicrograph, shows crystallization spread through about half of the glass. Numbers 39 and 40 were similar to number 38, number 40 having much less opacity.

Number 41, 42, and 43 grade to a clearer glass with 43 being the clearest. The x-ray diffraction data of numbers 32 through 37 for the most part gave an amorphous pattern with a few lines with a 'd' value from plus 4 through 8 which did not fit any substance in the A.S.T.M. tables. Number 32 gave faint lines for quartz ( $d = 3.33$ )  $I_0 = 0.7$ ; number 32 gave a line  $d = 3.25$  of  $I = 0.9$ .

TABLE V

Comparison of Diffraction Data of Numbers 38 Through 43

<u>Sample</u>	<u>I of Quartz Peak, <math>d = 3.33</math></u>	<u>I of Cristobalite <math>d = 4.0</math></u>	<u>Temperature (deg. C.)</u>
38	0.7	0	1400-1000 and cooled at room temperature.
39	0	1.0	#38 heated to 1100°C, cooled at room temperature.
40	0.9	0	quenched at 1300°C.
41	0	0	quenched at 1340°C.
42	0	0	quenched at 1375°C, hint of $\text{CaF}_2$
43	0.5	0	treated same as #38

TABLE VI

Comparison of Numbers 44 Through 75, All of Glass Batch 4n

Sample	I of Quartz Peak (d = 3.33)	I of NaF Peak (d = 2.32)	Temp. °C.	Description
44	56.0	2.7	Raw Batch to 600	Resembles raw batch
45	29.2	5.5	800	white lumps resembling pumice or scoria
46	16.0	2.7	850	Fair opal
47	2.7	0	900	See photomicrograph, about $\frac{1}{2}$ crystal.
48	1.11	0	960	Same as 48, see photo.
49	---	0	1000	About $\frac{1}{2}$ crystal, see photograph
50	37.3	4.5	Raw Batch to 675	Calcined lumps or raw batch (see 44)
51	19.4	4.0	700	Between 44 and 45.
52	19.2	3.4	760	Similar to 45.
53	29.7	4.5	775	Similar to 45.
54	21.0	3.0	810	Similar to 45.
55	11.0	1.5	860	More glassy than 45, see photomicrograph
56	20.0	0	910	Similar to 55
57	6.2	0	960	Milky and somewhat trans- lucent to slightly clear.
58	3.0	0	1020	Less opaque than 57
59	3.4	0	1060	Less opaque than 58
60	1.1	0	1060	Clear, see photo.
61	-	0	1100	About $\frac{1}{4}$ crystal
62	-	-	1120	Clearer than 63 with sparse crystal specks
63	3.6	1.0	1120	As in photo, bubbles, partially crystal.
64	0.6	0	1180	As in photo
65	4.7	-	1100	Similar to 64
66	1.2	0	1140	Similar to 64
67	-	0	1050	Similar to 60
68	-	0	1050	Similar to 60
69	-	2.1	720	Clear before heated, good opal after, see photo.
70	-	1.5	820	$\frac{3}{4}$ crystal, rest clear
71	-	0	920	Approaching clear, $\frac{1}{4}$ crys- tal, similar to 67
72	0.7	-	1055	clear with seeds
73	-	0	430	Clear before heating, $\frac{1}{2}$ opal after.
74	0	0.6	550	See photomicrograph
75	0.6	1.6	620	Good opal, see photo.

In using the direct current circuit the three variables of temperature, current, and voltage causes difficulty in ascertaining how the glass behaves with change in temperature. Therefore, the resistance equal to  $\frac{E}{I}$  was calculated.

TABLE VII

Direct Current Circuit, Change of Resistance With Change in Temperature

Run #2

<u>Raising Temperature</u>		<u>Lowering Temperature</u>	
<u>Temperature</u>	<u>Resistance</u>	<u>Temperature</u>	<u>Resistance</u>
<u>(deg. C.)</u>	<u>(Ohms)</u>	<u>(deg.C)</u>	<u>(Ohms)</u>
552	Infinity	1000	34.3
570	6880	960	37.2
586	2700	940	44.5
600	1300	920	51.2
618	545	900	50.0
260	409	870	77.2
626	325	860	73.6
656	142	850	77.2
662	103	840	77.2
666	67.5	820	79.6
804	49.0	800	77.2
816	42.0	780	70.2
866	35.8	760	65.8
966	29.7	730	64.2
980	28.6	720	64.2
1000	30.3	700	62.2
		680	51.8
		660	76.6
		640	82.8
		620	92.3
		600	105.9
		580	172.0
		560	420.0
		540	766
		520	1370
		500	2450
		480	5560
		470	17000
		460	Infinity

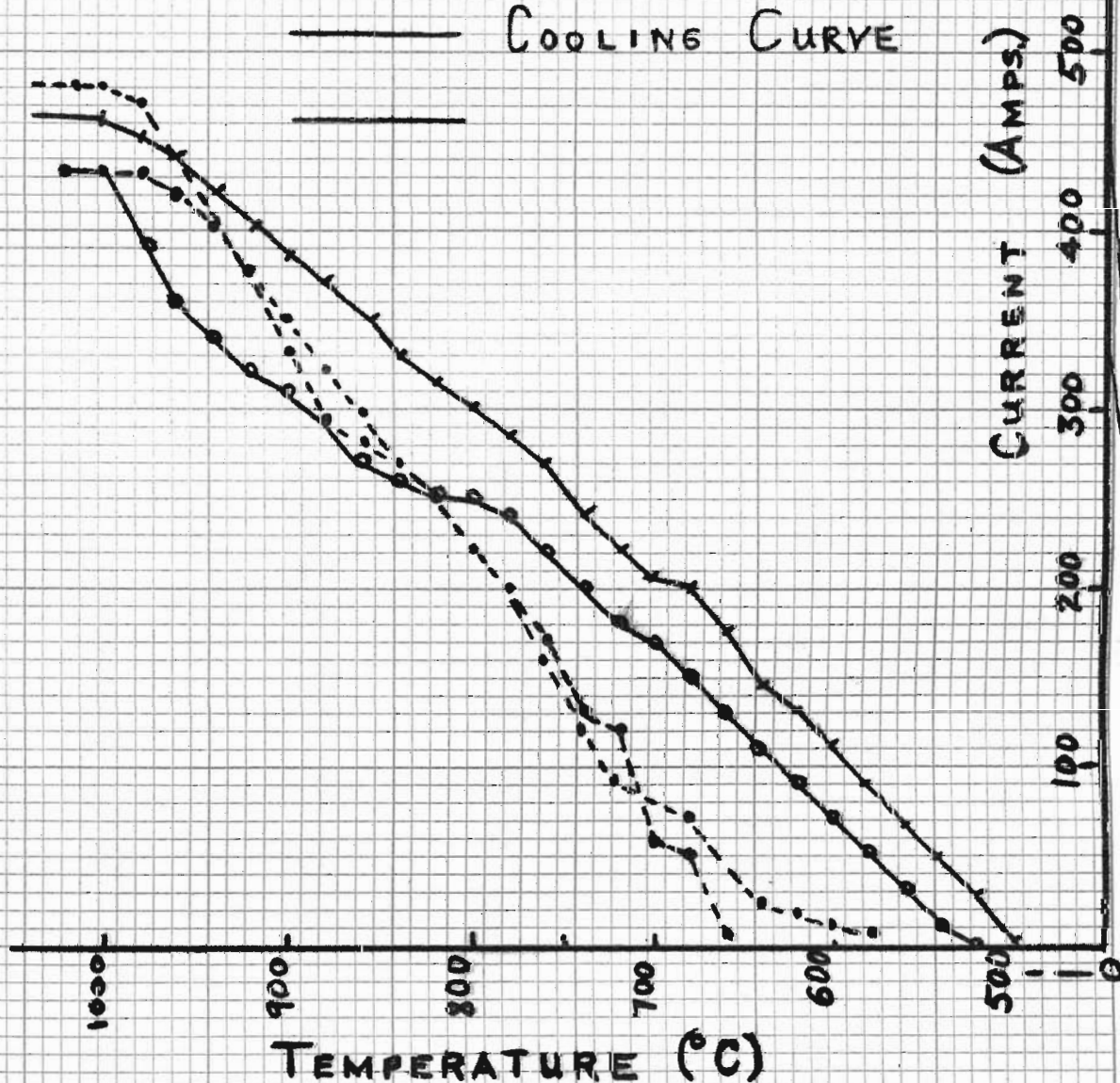


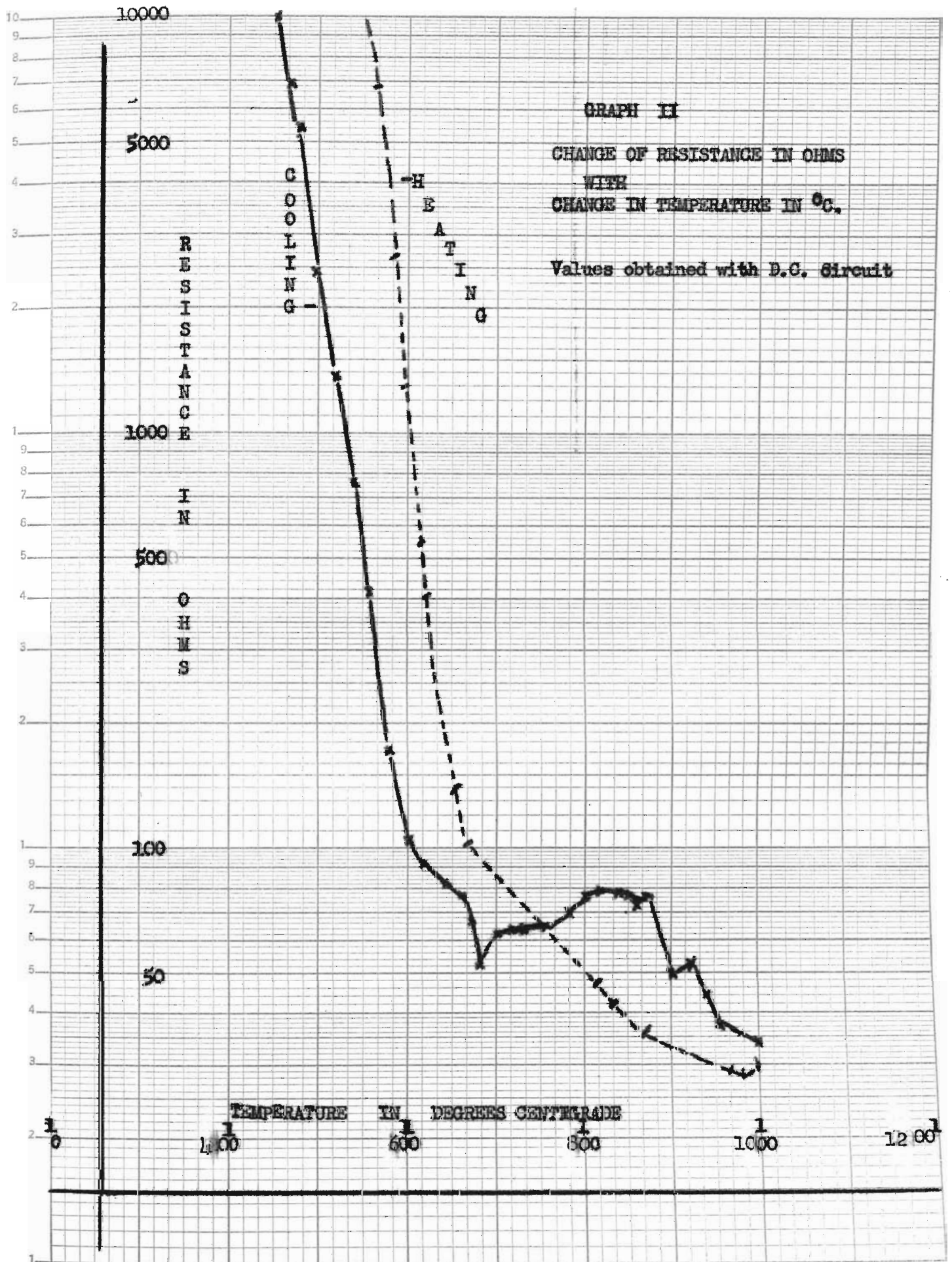
# GRAPH I

Change of Conduction (Amps)  
with  
Change of Temperature (°C)

[DATA FROM A.C. CIRCUIT]

----- HEATING CURVE  
——— COOLING CURVE

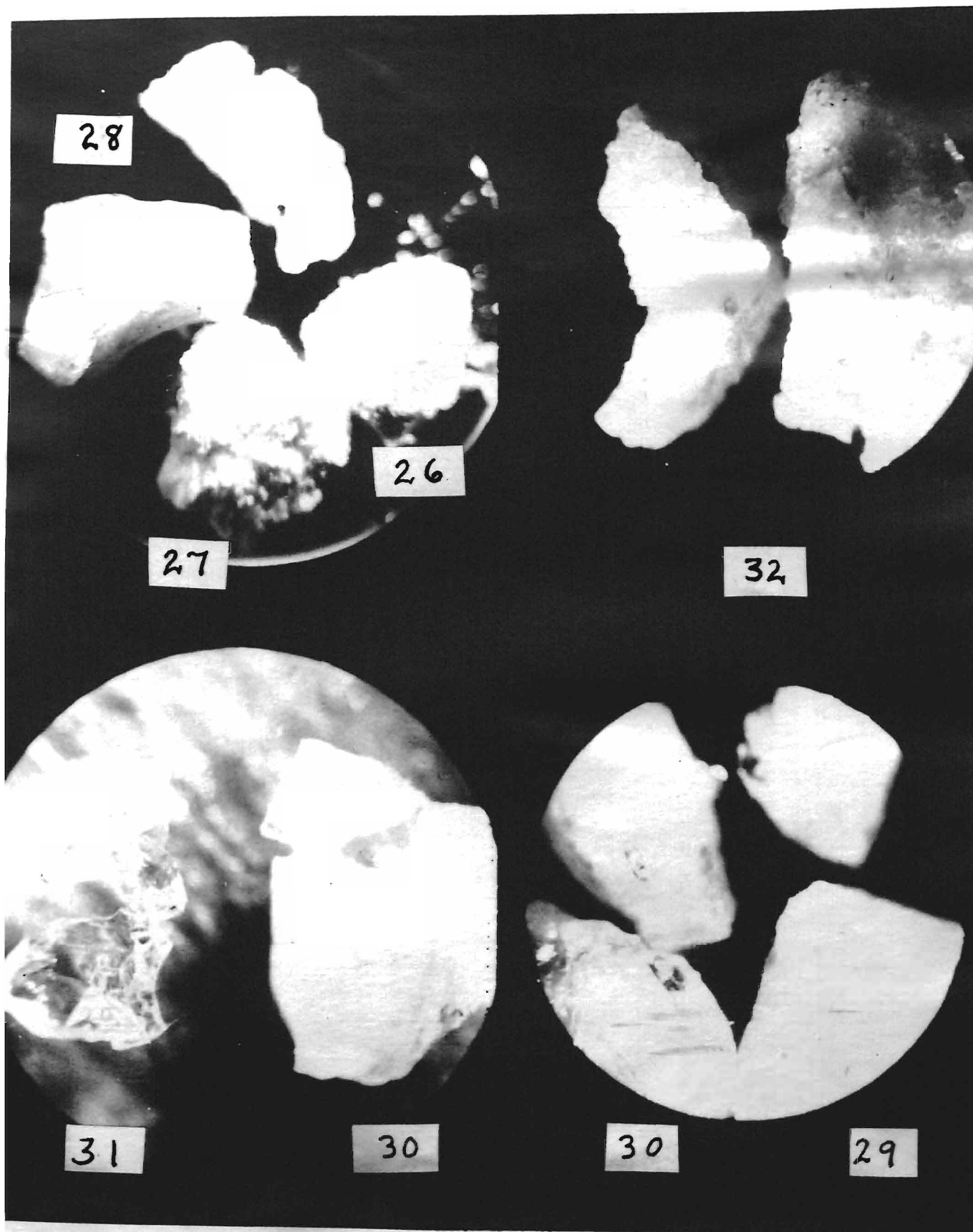




The following five pages contain photomicrographs of glass samples number 8, 9, 19, 23, 24, 26, 27, 28, 30, 31, 35, 37, 38, 43, 44, 48, 49, 50, 55, 56; 59, 60, 63, 64, 67, 69, 74, and 75.

Various magnifications up to 500x - 800x were tried on a research metallograph. The best results obtained were with a magnification of approximately 50x. The larger magnifications did not show up well as the particle size of the material causing opacity was beyond the range of a microscope. The photomicrographs were taken to show the formation of the opacity and gives a much better description of the glass than a mere word picture could give.



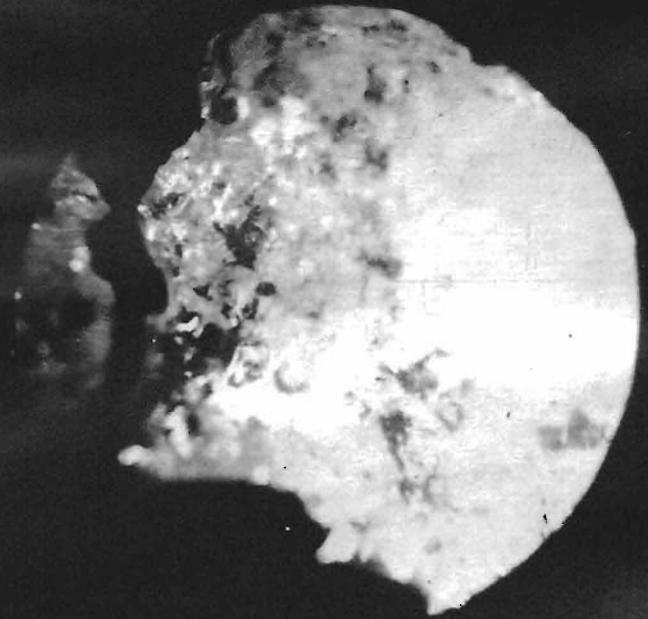




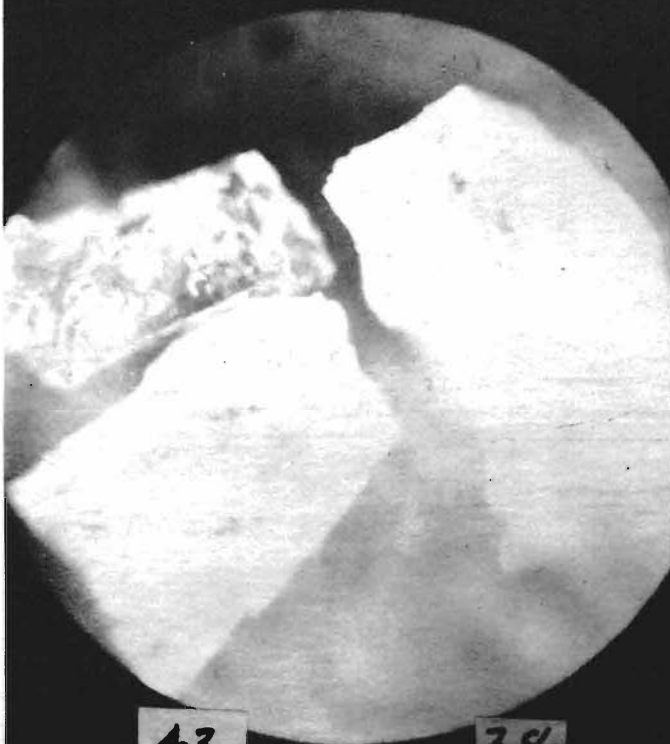


37

35



38



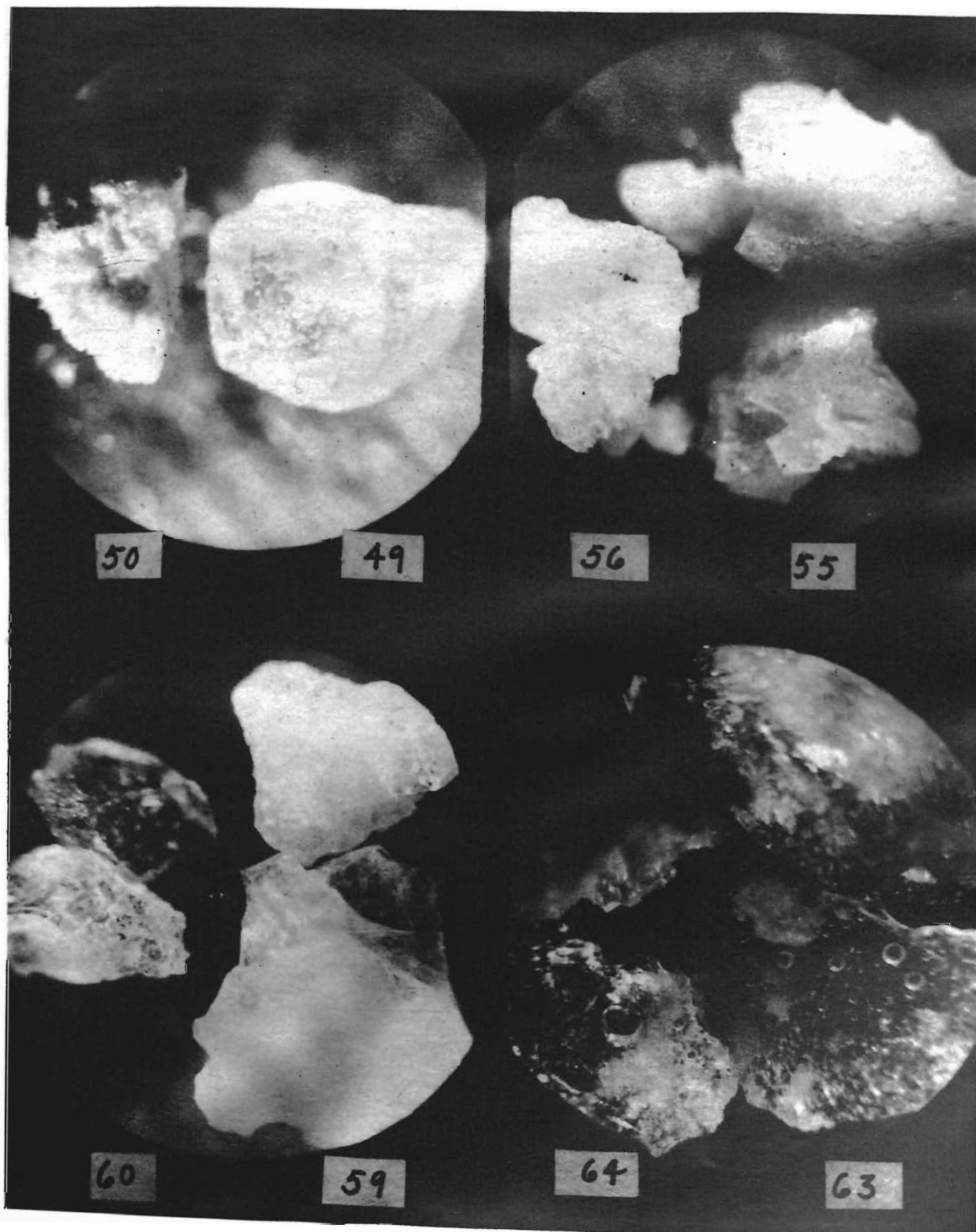
43

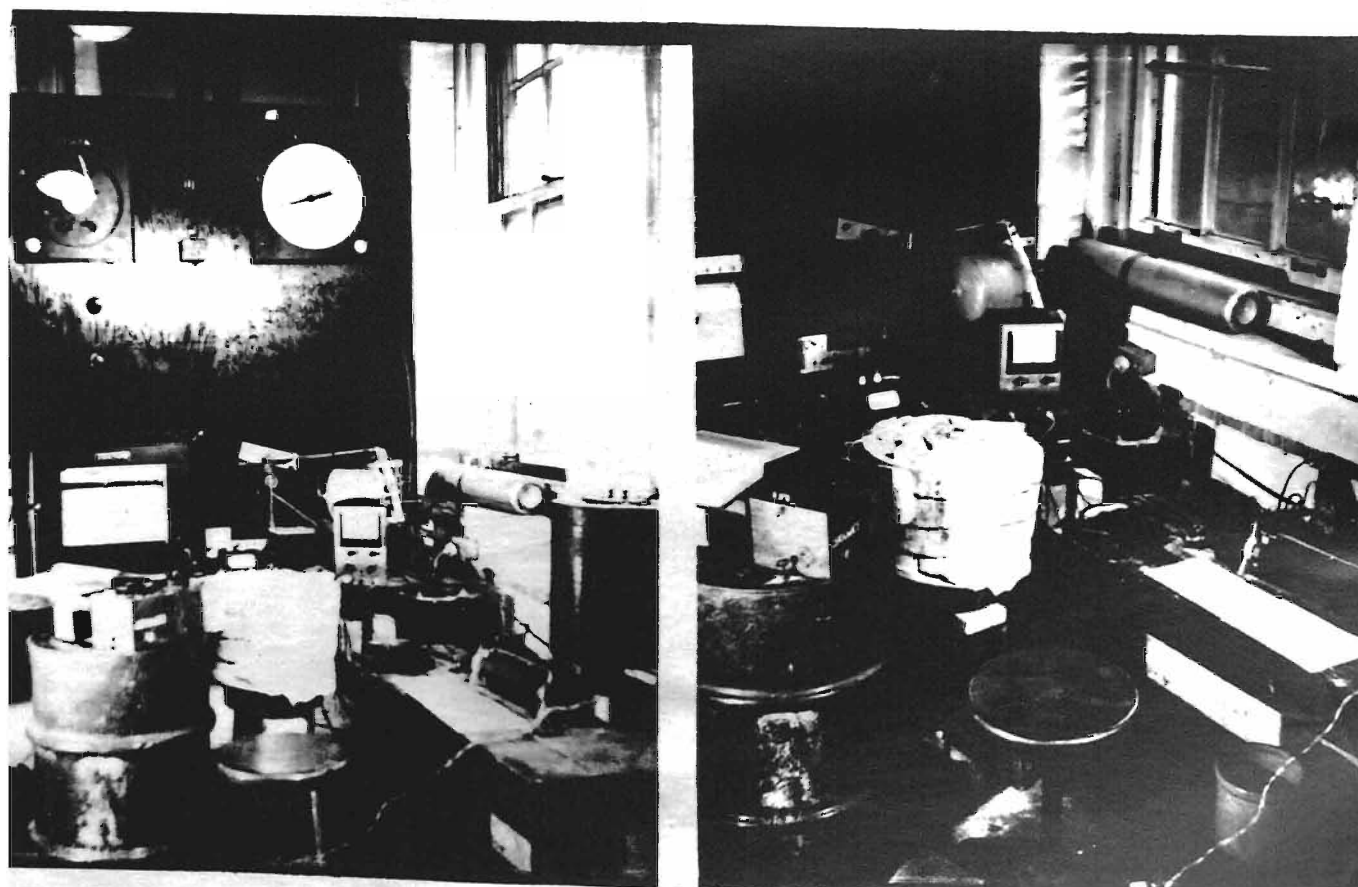
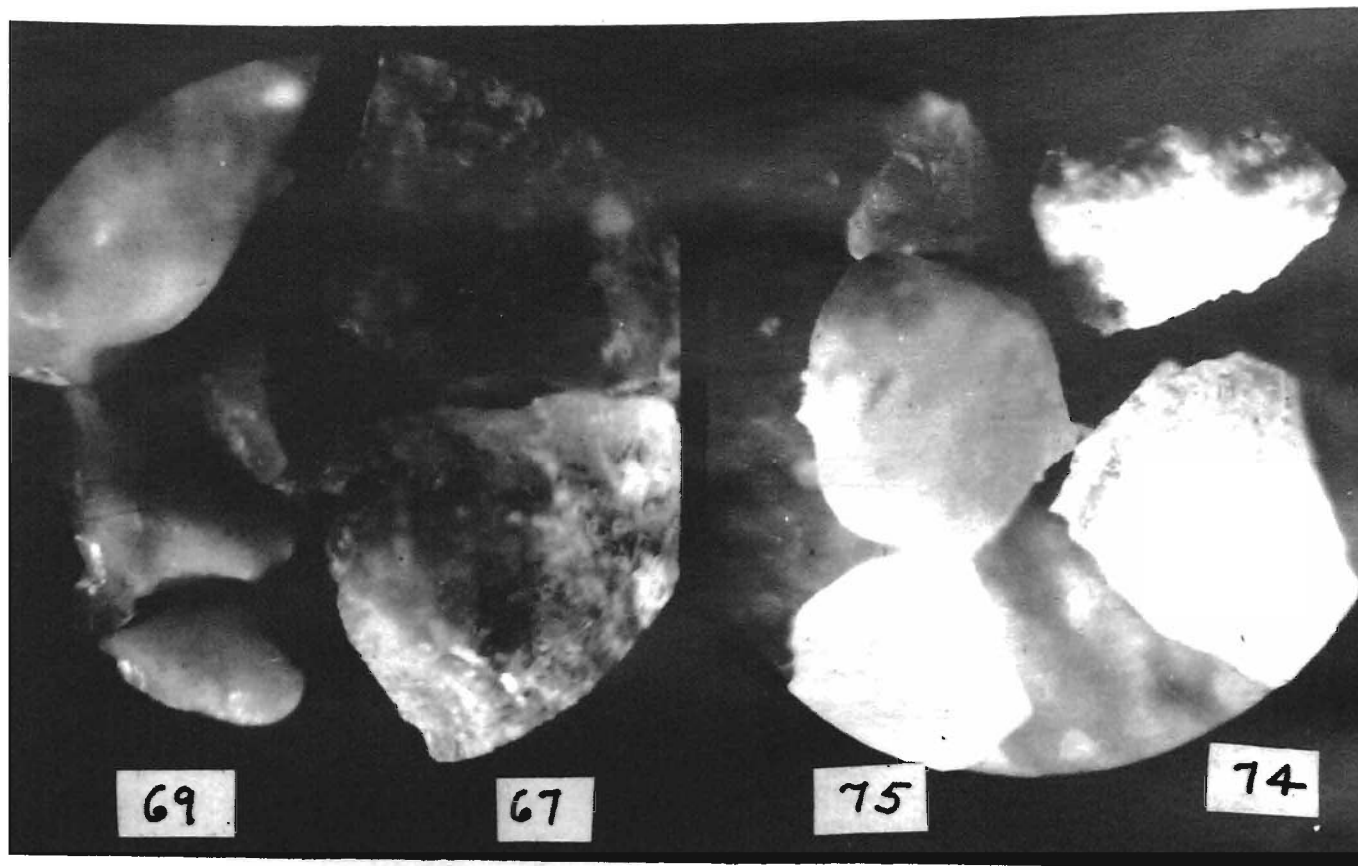
38



48

44







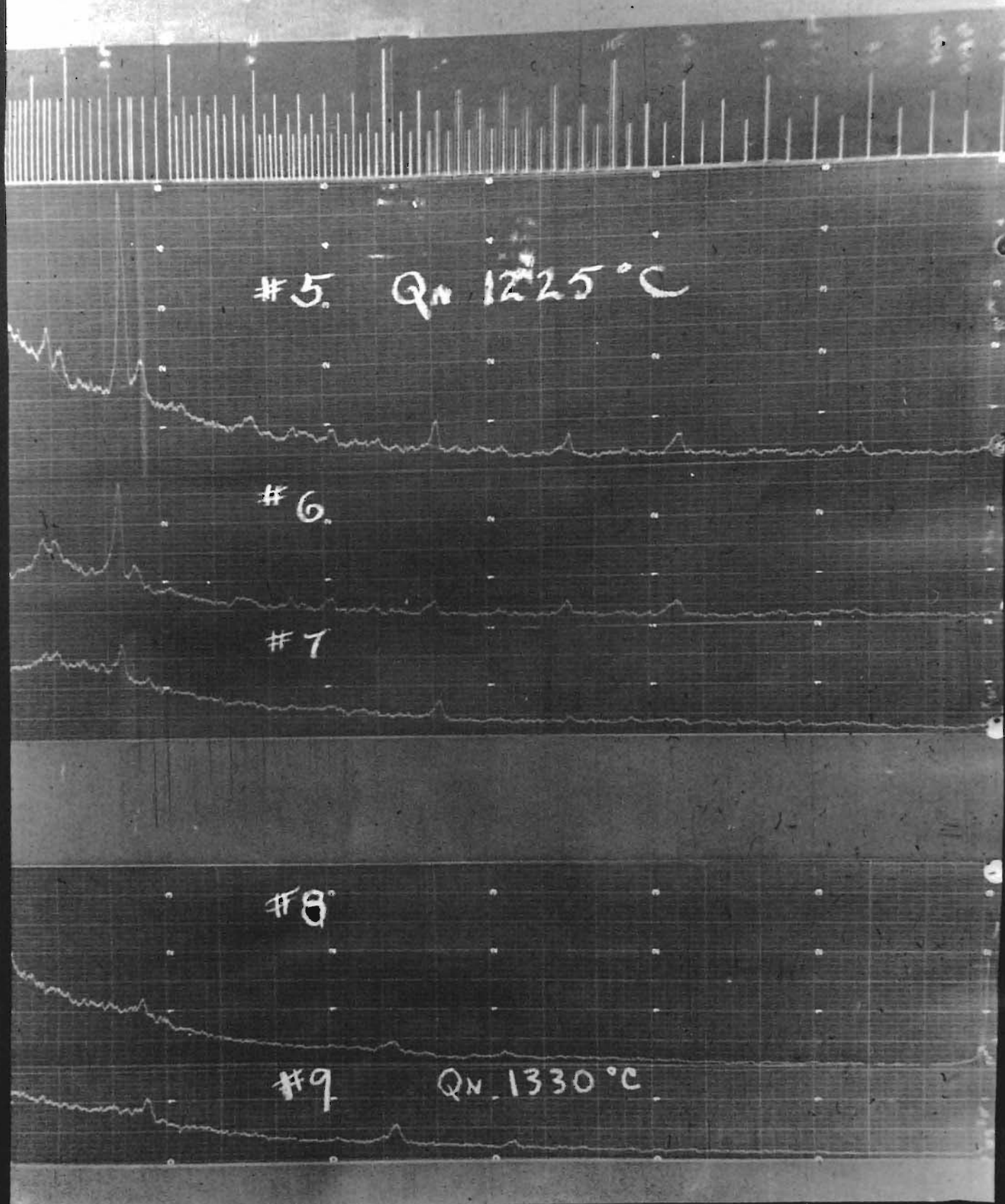
The following 15 pages contain reproductions of the x-ray diffraction patterns run on glass samples, numbering 1 through 75.

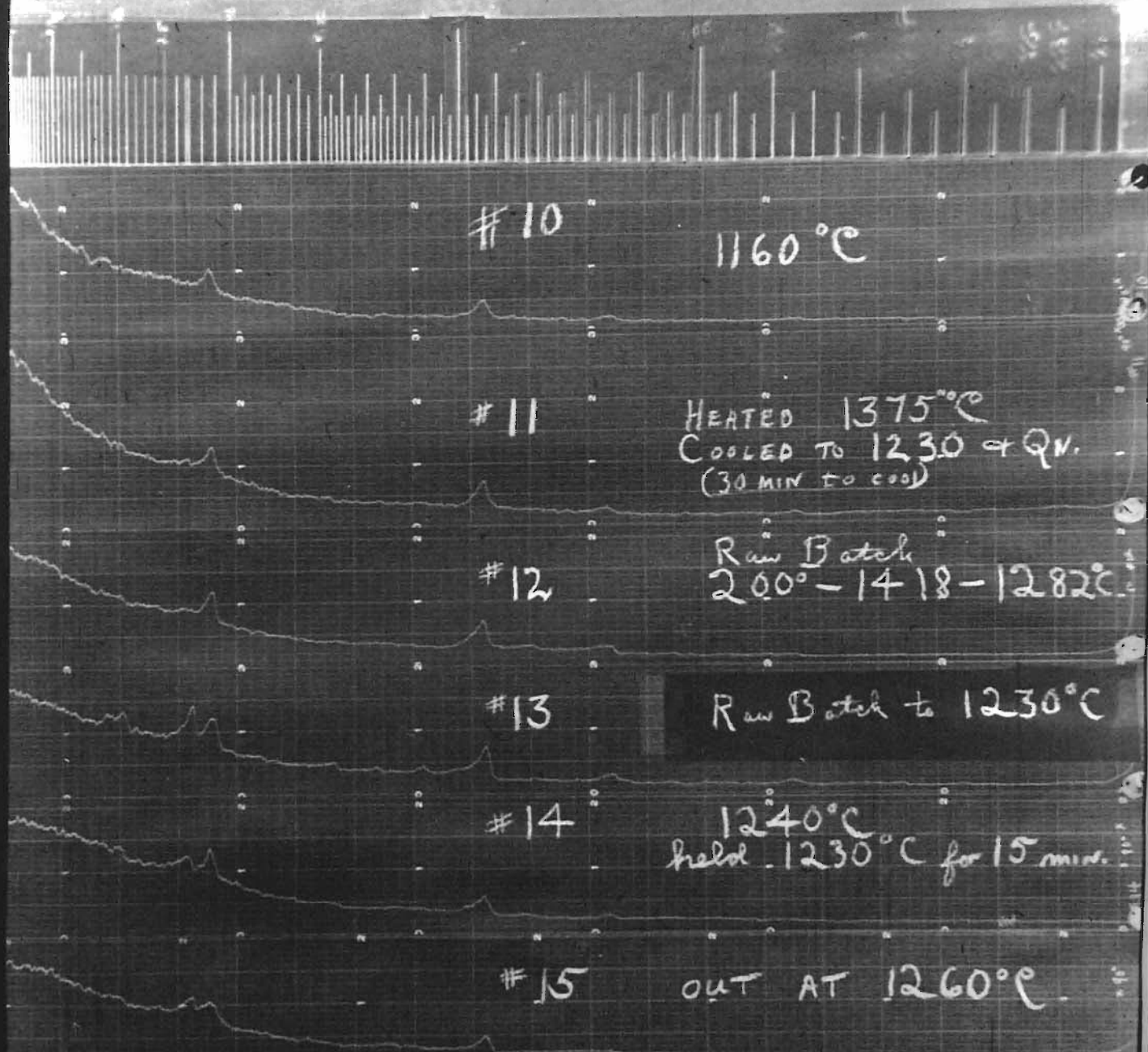
#1 Temp 20 - 900°C

#2 Temp. 20 - 1000°C

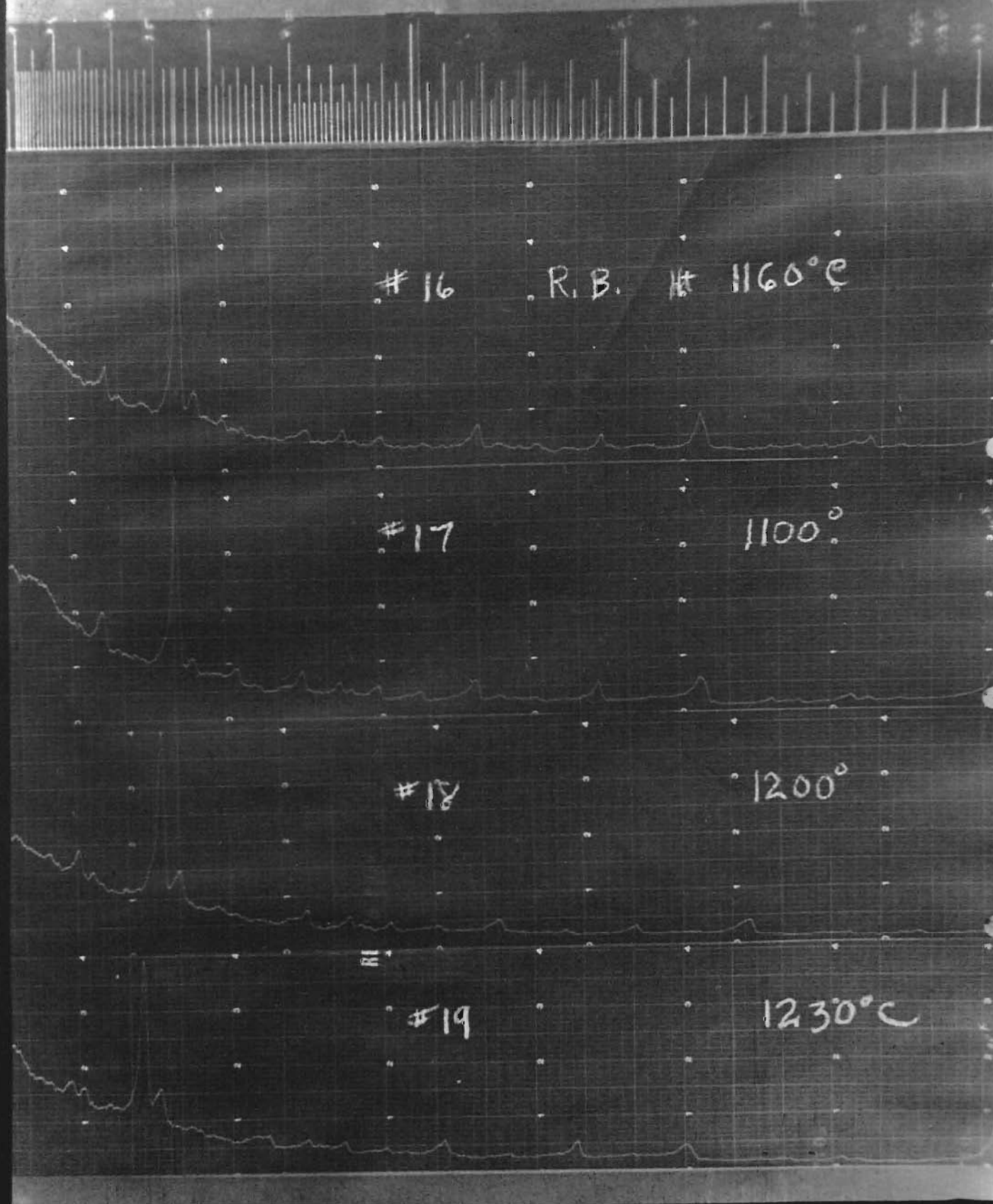
#3 QUENCHED at 1100°C

#4 QN @ 1200°C









4c

#20

1280°C

#21

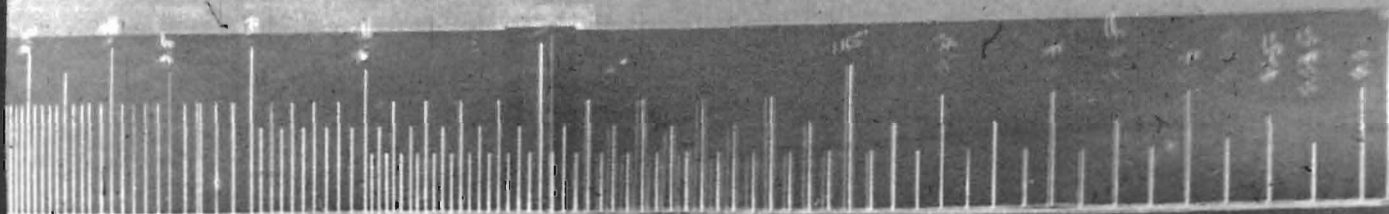
1300°C

#22

1330°C

#23

1375°C



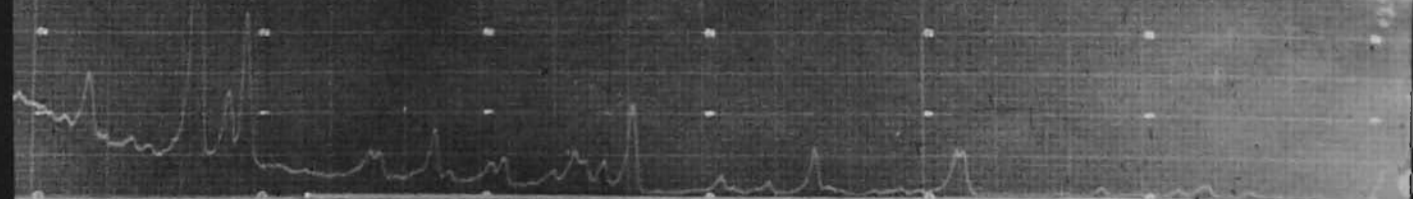
#24

700°C



#25

400 810°C



#26

900°C

#27

1000°C

#28

1100°C

#29

1150°C

#30

1300°C



#31

1350°C

(clear glass)

1360-1325

#32

1360°C NOT QUENCHED  
(clear)  
ALLOWED TO COOL IN ATMOS.

#33

1360-1300°C

#34

#35

1210° cooled

clear

#36

1200 cooled  
w/out QN.

clear

#37

1310° cooled  
w/out QN

clear



#38 1400 to 1000° in Kiln  
then air cooled

#39 #38 to 1100°C  
- Cooled w/out QN

#40 QUENCHED @ 1300°C

#41 #40 QN at 1340

#42 QN AT 1375°

#43 #42 TREATED  
SAME AS #38

#44

RB 4N #TEO

600°C

#45

800°C

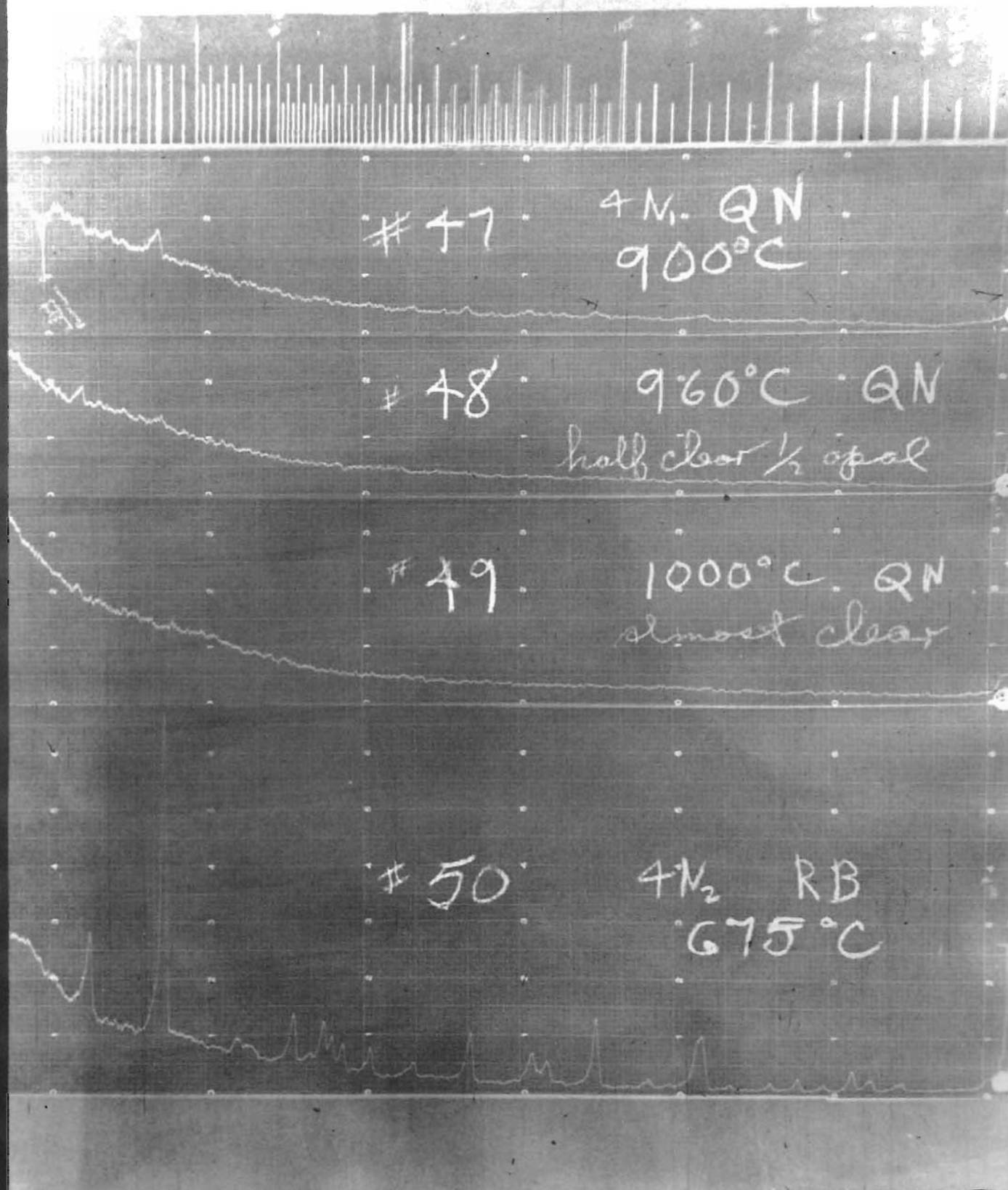
#46

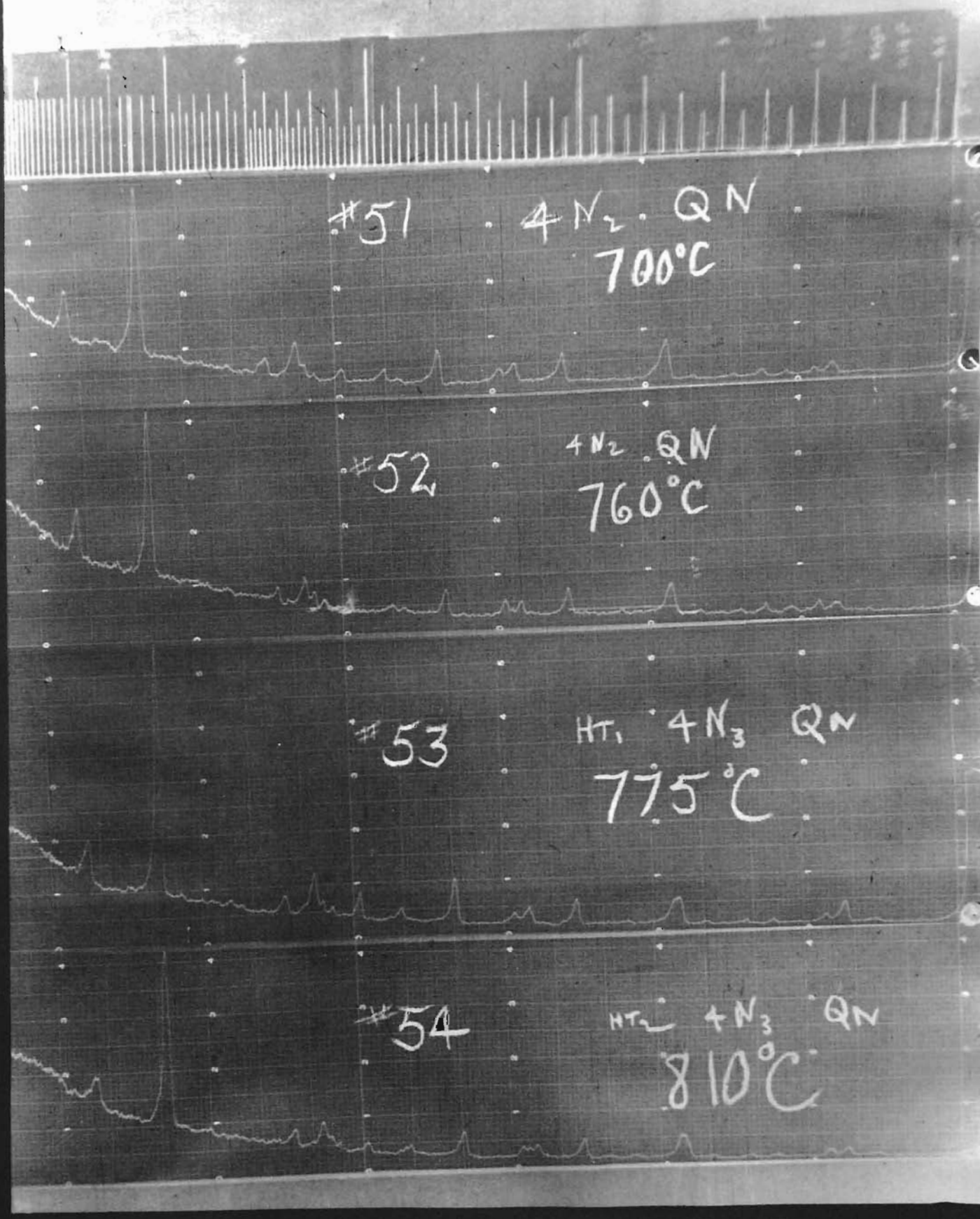
#45 at 850°C

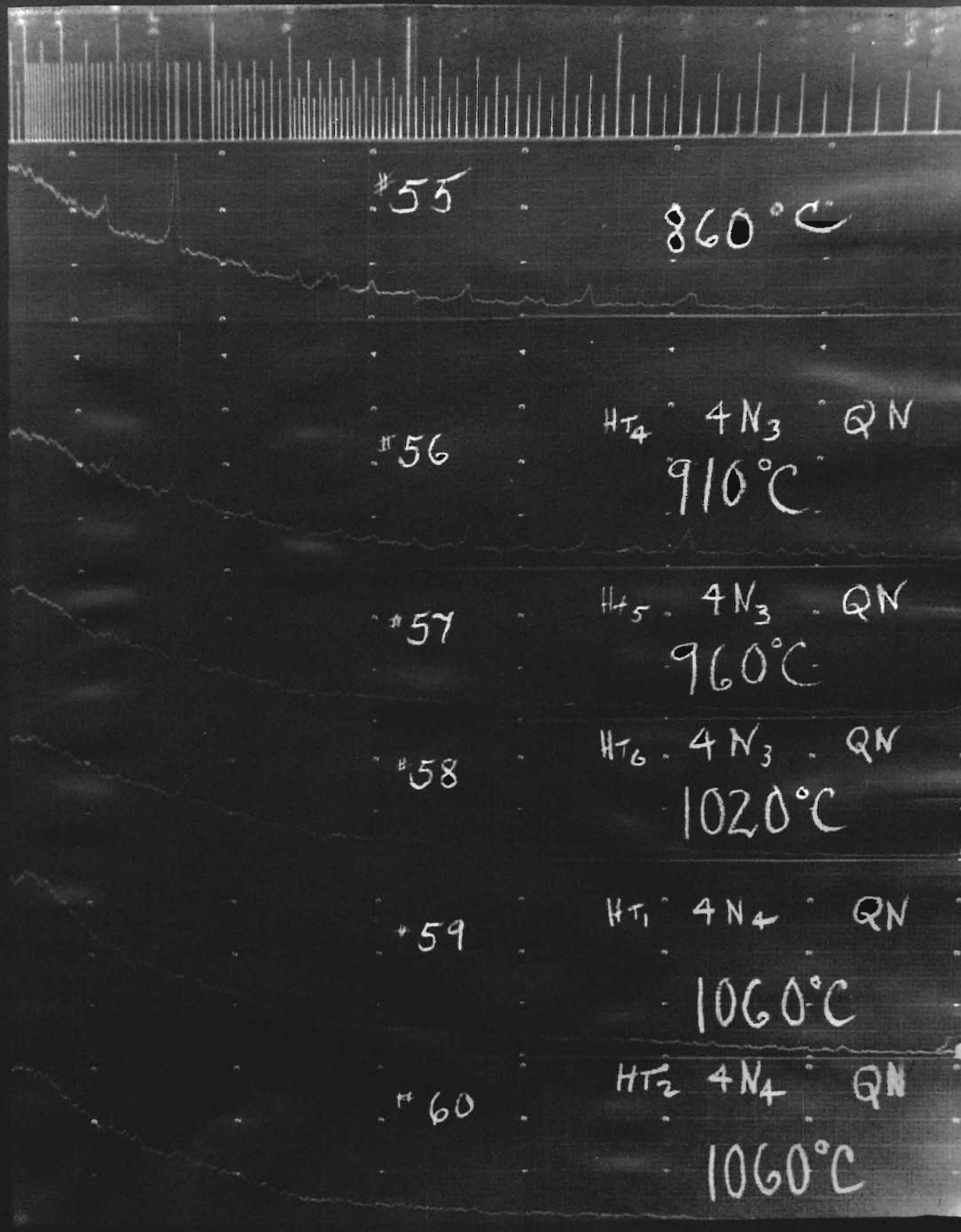
IS OPAL

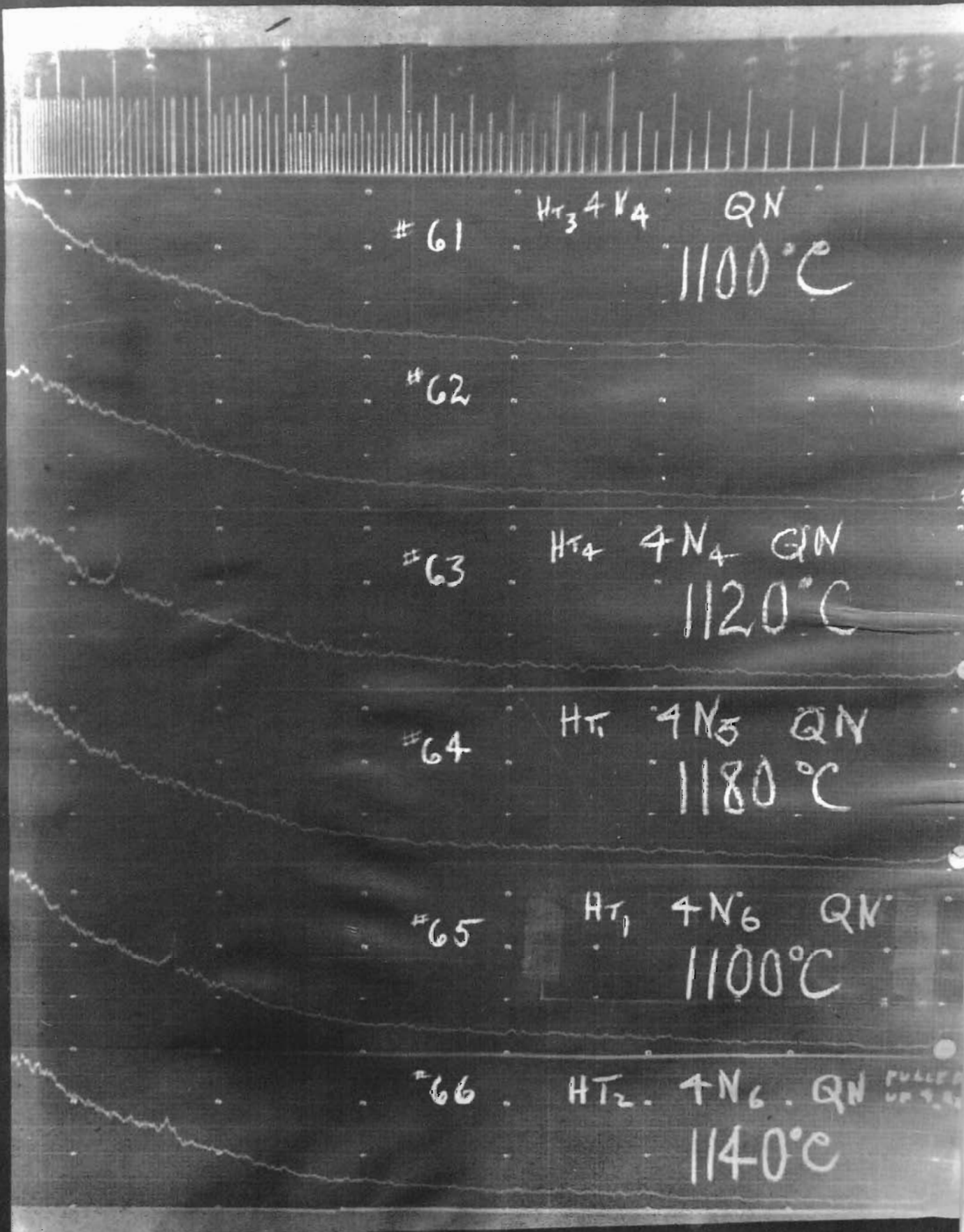
EXPANDED &  
RAN OVER



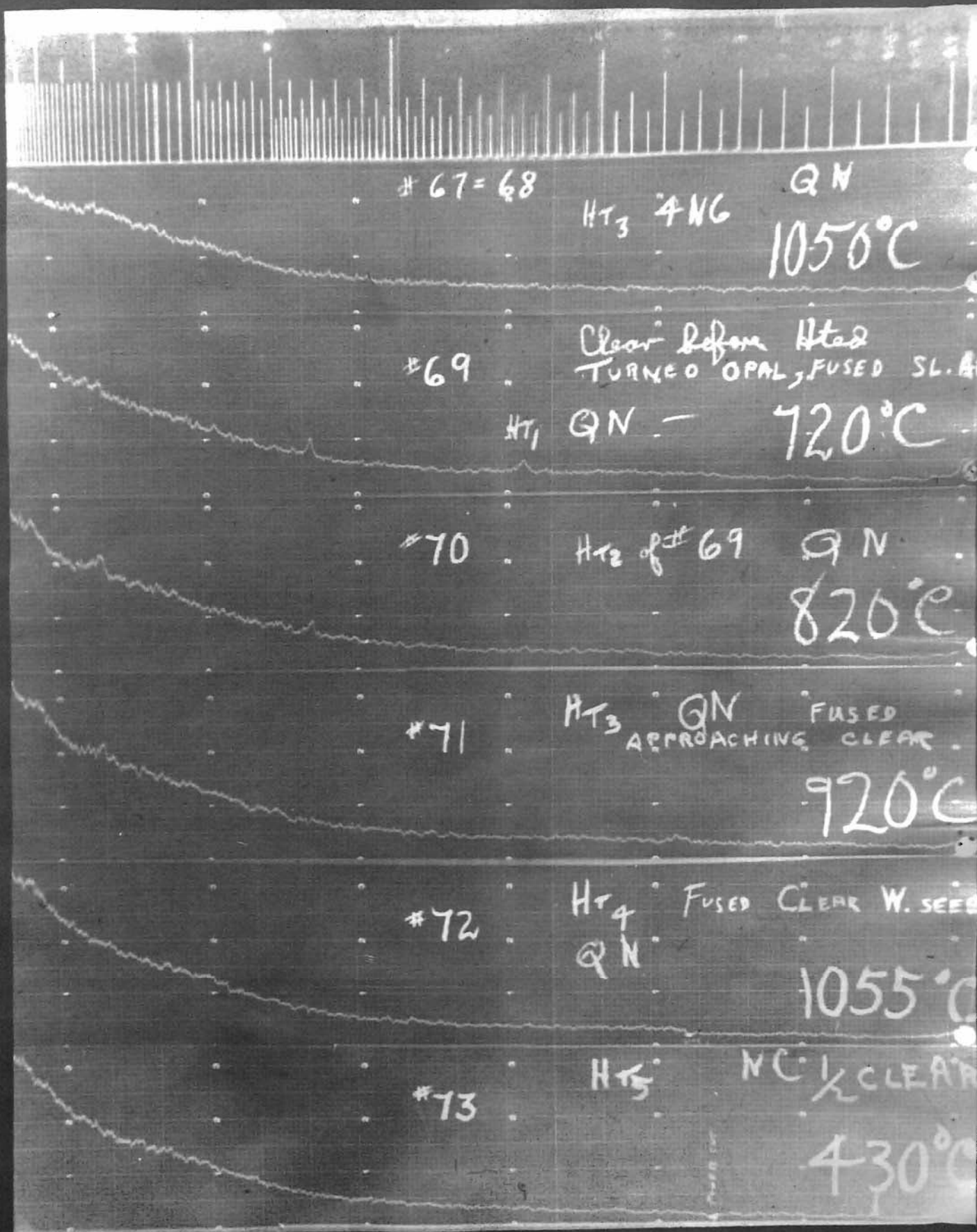




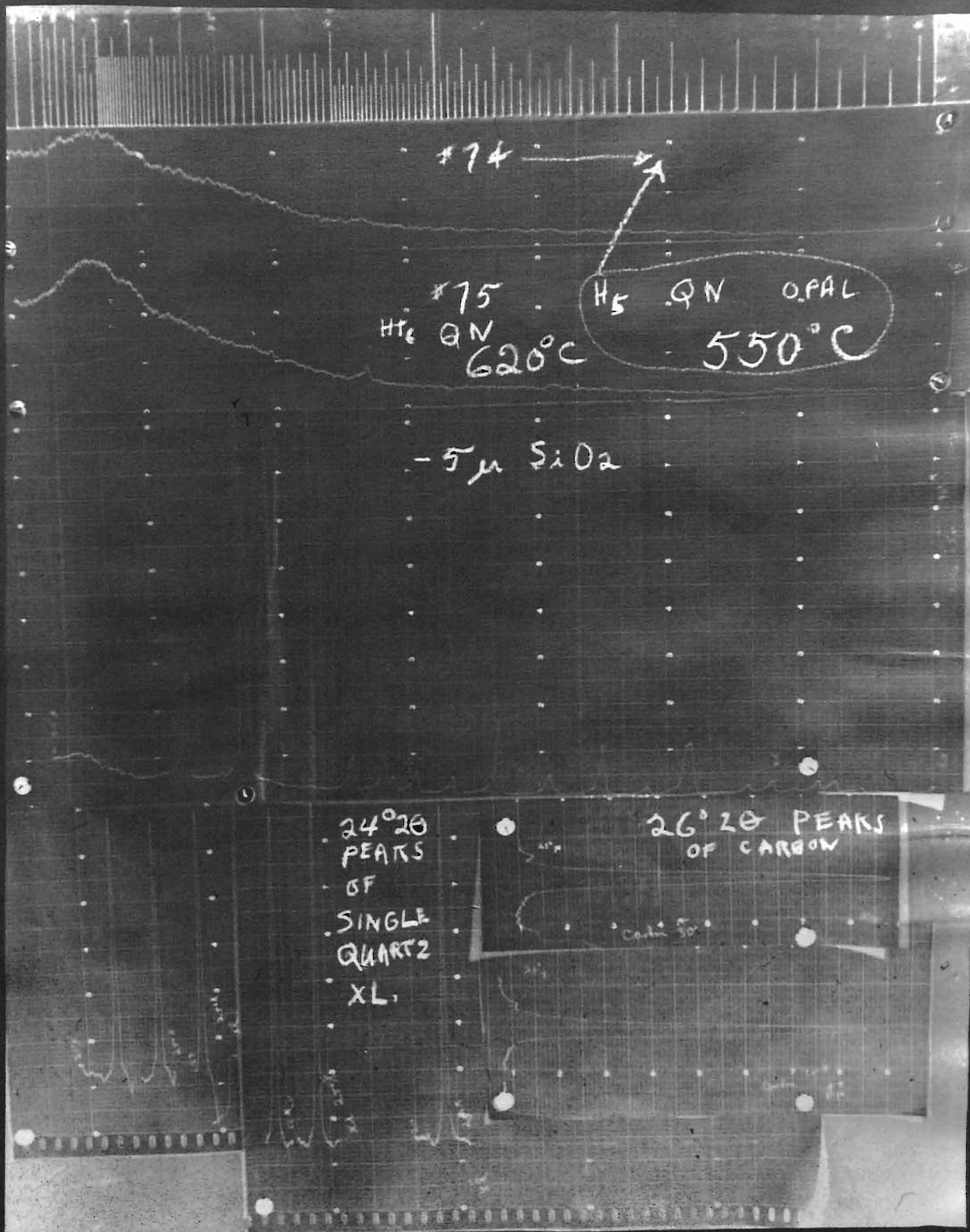












## SUMMARY OF RESULTS AND CONCLUSIONS

1. In order to use a differential thermal analysis for a determination of the temperatures of nuclei formation or crystal growth in opal glass, a standard must be used as identical to the properties of the sample glass as possible while keeping the standard a clear glass within the limits of the heating and cooling used in crystal formation of the sample glass.

2. From the x-ray data of runs number one through seven (Table III), the amount of quartz decreases with an increase of temperature from 900°C to 1100°C, increases from 1100°C to 1200°C, and decreases from 1200°C to 1400°C at approximately the same rate as the decrease of quartz with a temperature rise from 900°C to 1100°C. The following is an explanation of this phenomena:

(a) The fritting to a clear glass caused formation of quartz crystals less than 2000Å.

(b) Heating to 900°C caused the crystallites to rapidly regroup to form larger crystals of quartz.

(c) Heating to 1000°C means that above 870°C the quartz is unstable and the crystallites do not try to form quartz have a tendency to form tridimite, the quartz already formed tending to disintegrate.

(d) Heating to 1100°C therefore shows much less quartz.

(e) Heating to 1200°C is above the eutectic temperature of 1170°. Viscosity is lower and silica is the only crystal allowable. The crystallites have greater force toward the for-

mation of some crystal of silica. However, the rearrangement to form tridymite is so severe that quartz is formed.

(f) Heating to 1300°C causes some of the quartz to go into solution.

3. A possible method of giving the surface of an object formed from opal glass a metallic luster would be the use of wood in forming the glass, or causing pine to come into contact with the hot glass surface.

4. In a glass of composition such as 4n, the presence of about one-tenth the amount of quartz in the original batch will give a translucent milky glass, while the presence of NaF with a larger amount of quartz gives a dense opaque white glass.

5. The measurement of the variation of the conduction of electrical current through opal glass with a change in temperature does not give positive formation as to the temperatures of nucleation or crystallization. It does, however, give very good information as to the temperature at which the glass is molten. The semi-log graph of temperature vs resistance of data from the A.C. circuit indicates some type of change at about 675°C and at 900°C on cooling. The cooling curves, temperature vs. current, with the A.C. circuit are much less definite than the data from the D.C. circuit.

6. A clear NaF glass can be made opalescent or "flashed" at temperatures below the softening point of the glass but above the temperature at which the glass will pass a current by ionic conduction.

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## VITA

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